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Abstract

This final report describes work done on validation of the environmental-effects modelling system ECCES as applied to forest soils. A short description is given of a site in a Danish forest district where monitoring of dry and wet deposition, throughfall, litterfall and soil water composition is continuing since 1985. The present project is a supplement to this field investigation and has covered the following topics:

- Investigation of deposition and transport of heavy metals at the forest site. Analyses for Cd, Zn, Pb, etc. in precipitation, throughfall, litterfall and soil-water and in samples of the soil have been made using ICP-MS and other methods. The data are compared with similar data from the literature and are used to estimate the fluxes of heavy metals. The clayey soil is unpolluted and the concentrations in the soil water were mostly below the detection limits.
- Characterization of the soil to obtain data needed for the modelling of material fluxes in the system for major as well as minor elements. Cation exchange capacities as function of pH were measured for samples from four soil horizons. Distribution coefficients were determined for the Cd/Ca and Zn/Ca systems at various pH. Fitting with Langmuir or Freundlich expressions is discussed. Anion exchange capacities were low in this relatively high pH soil. Accelerated extraction of soil samples with weak sulphuric acid to obtain indications for the long-term development was also done.
- Development of a simple forest model coupled with the existing soil model and testing of the overall system using data from the field investigation and laboratory experiments. Simulation of material fluxes of major components in the forest system were in reasonable agreement with the measured values, taking some rather coarse assumptions in the model into account. Time did not permit the introduction of various improvements indicated by the experimental work. Modelling of the turn-over of heavy metals was not attempted. Example calculations simulating soil development over long periods are presented. Qualitatively the development is thought to be correct, but further work is needed to improve confidence in the results. A more flexible version of the model is under development.

The project was carried out as a cooperative effort between the Danish Forest Experiment Station (SFF), Danish National Environmental Research Institute (DMU) and Risø National Laboratory. It was supported by grants from the Danish Ministry of Energy.

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Sections 1 and 4 are supplied by the Systems Analysis Department, Risø.
Sections 2, 3.2. and most of 3.3. by the Danish Forest Experiment Station (SFF)
Section 3.1. by the Danish National Environmental Research Institute (DMU)
Sections 3.4. to 3.5 by the Chemistry Department, Risø.

1. INTRODUCTION and PURPOSE

The development of the environmental impact model ECCES began in the early eighties and was supported by Research Programmes of the Ministry of Energy (EFP-82, EFP-84, EFP-85 and EFP-87). The aim of this work was to describe the effects of anthropogenic emissions such as sulphur dioxide and nitrous oxides on the environment. The model has been described in a number of reports, see for example /1/.

When undergoing chemical changes in the atmosphere these emissions acidify the precipitation or form components which later contribute to soil acidification. The result could be severe damage to the environment, for example to trees and other vegetation, either by direct action of the acidified precipitation or dry deposited gases or due to changed soil properties such as increased mobility of heavy metals and mobilisation of aluminium ions. The chemical changes in the soil can also induce changes in the microfauna.

Recent work on the model has been concentrated on the sub-models for plant uptake (forests) and for calculation of changes in soil properties under acidifying circumstances.

The present report is the final report of the EFP-87 project: "Application of the soil chemistry model to forest soils". The project represented the first attempt to use the model on "in vivo" conditions by comparing modelled and measured soil water concentrations. Development of a forest model and at least a partial validation of the model was one purpose of the project. Another more experimental part of the project has mainly been concerned with measurements of soil chemistry properties and with heavy metal analyses of soil, soil water and litter. Data - which are new for Denmark - are reported for heavy metals in leaf or needle litter from beach and Norway spruce, respectively. Experimental methods and some of the measurements are described in greater detail in the halfway report for the project /2/.

The project was carried out as a cooperative effort between Risø National Laboratory, the Danish Forest Research Institute (SFF) and the Danish National Environmental Research Institute (DMU).

The project is associated with a larger and older experimental research project concerning ion balances in forest ecosystems. This latter project supplied most of the data utilised in the present report on the macro chemistry at the experimental test site(s). It is run by SFF and DMU financed by special grants, and comprehensive results are reported elsewhere, see for example /3/.

1.1. The ECCES model.

As an introduction to the general capabilities of the ECCES model the structure of the model with the most important modules is shown in Fig. 1.1. These modules will be described briefly in the following.

Emission sources are described in the model as either point or area sources. Area sources are used to describe emission from a large number of point sources distributed more or less uniformly over a specified area such as towns or roads. Area sources are assumed to emit at heights up to 10 metres, while point sources consist of a single strongly emitting source higher than 10 metres such as a power plant. The emissions may consist of various substances and the present version of the model is able to deal with up to fifteen, including heavy metals.

Dispersion is calculated on the basis of meteorological data, which are long-term averages of stability categories, wind speeds, wind directions and precipitation. The model calculations are based on a plume model /4/, in which the horizon is divided into 12 sectors each covering 30 degrees. Using a library of meteorological data, the weather characteristics in each sector are calculated and hence the dispersion of pollutants in the sector.

Deposition of a specific pollutant is characterised by a deposition velocity that varies with the chemical form of the pollutant. In the atmosphere SO_2 is transformed to H_2SO_4 (or ammonium sulphate). These two different forms of sulphur have different deposition velocities. The transformation of SO_2 to H_2SO_4 or NO_x to HNO_3 is calculated by the model. Deposition is also dependent on the precipitation which is incorporated in the model as monthly averages.

The latest development to the model is the forest module. A forest has a large surface roughness and because of this the deposition in a forest area is substantially larger than the deposition on open land. Besides taking this into account the forest module calculates interception and litter decomposition.

Litter decomposition is calculated on the basis of the previous year's loss of leaves, needles and branches. The litter will contain a certain amount of nutrients and other ions taken up by the trees which will be recycled in the ecosystem by the decomposition.

Accumulation in stems etc. due to forest growth or effects of thinning and similar can only indirectly be handled by the present model.

Soil chemistry and hydrology are closely interrelated. Precipitation reaches the ground and causes a change in the ion composition of the soil water. This leads to changes in the amounts of ions fixed on the soil matrix and a new equilibrium is established. The percollation of water through the soil layers carries the soil water further down into the deeper soil layers and leads to changes here also. These mechanisms are included in the model under the assumption that the soil layers can be described by a set of overlaying compartments and that equilibrium is established in each soil layer before the excess soil water percolates to the next soil layer. The hydrology model of the root zone is simple: percolation is supposed to take place when and only when the field-capacity is exceeded.

Uptake of pollutants in crops or trees is based on the soil water concentrations. In addition the uptake is assumed to depend on the amount of water taken up by the crops or trees and on certain other factors which can discriminate against or favour the actual uptake of specific ions, for example essential nutrients can be taken up actively. The crop can be harvested and hereby ions and nutrients will be removed from the system. Ions and nutrients may also be recycled with the litterfall from the trees followed by decomposition of the organic material.

It is only the forest module and the soil chemistry module which are utilized in the present context. Deposition from the atmosphere is introduced in form of experimentally determined average values for the test area. Due to the rather long time steps and to the average data used the model should preferably be run for relatively long periods. Since the available data only covers a relatively short timespan (~1 to 5 years) this may give rise to discrepancies. However, as long as the change in soil properties are not extreme this may not be a serious objection. The comparison of the model results with experimentally determined composition of soil water is thought to be of great interest as a demonstration of the "reasonableness" of the model assumptions. Unfortunately time has not permitted implementation and testing of various possible refinements of the model identified during the experimental work.

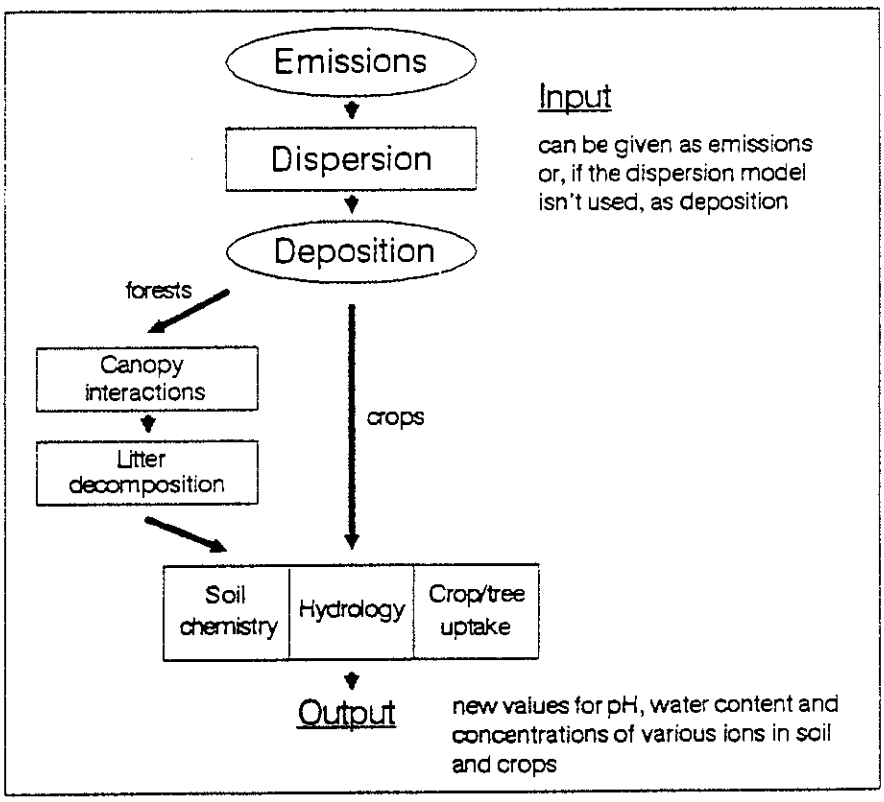

Fig. 1.1. The structure of the ECCES model.

2. DESCRIPTION OF TEST AREA

The test area utillized in this study is situated about 20 km from the shoreline of North Zealand.

The test area in North Zealand together with an area in Western Jutland make up the field sites of the project "Ionbalance in forest Ecosystems" which has been going on since 1985 as a cooperative effort between SFF and DMU. This project, in the following designated "the main project" has in short the following aims : To determine the degree in which Norway spruce and beech influence the podzolization process in relation to the acidifying effects of wet and dry deposition.

The results presented here for use in this subproject are only from the area in North Zealand.

2.1 Vegetation and previous use.

The test site was laid out as part of a species trial experiment /5/, see Fig. 2.1. The planting was done in 1965. The area was arable land before plantation. It was not and has not been fertilized in conjunction with the forest cultivation.

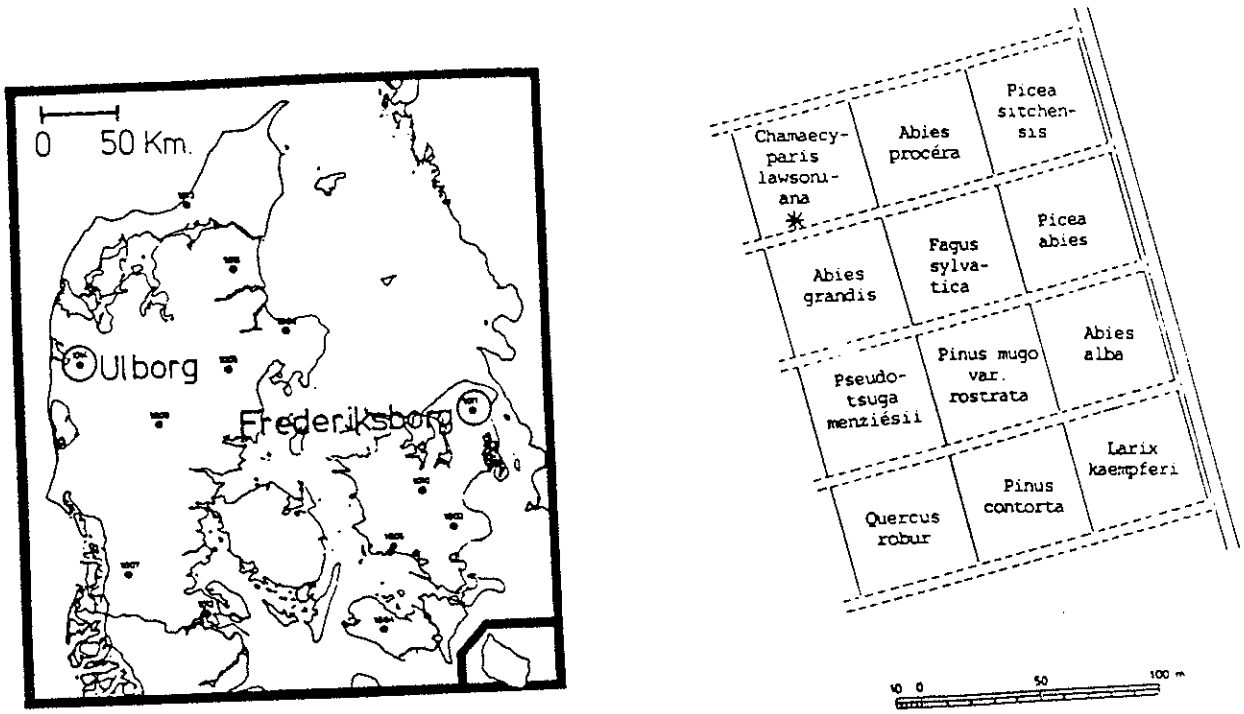

Fig. 2.1. Location of the experimental plots Ulborg in Western Jutland and Frederiksborg in North Zealand. The plantation system is shown to the right. Only the plots with beech (Fagus sylvatica) and Norway spruce (Picea abies) are included in this experimental programme. The * indicates the clearing in which "the outside forest measurements " are taken.

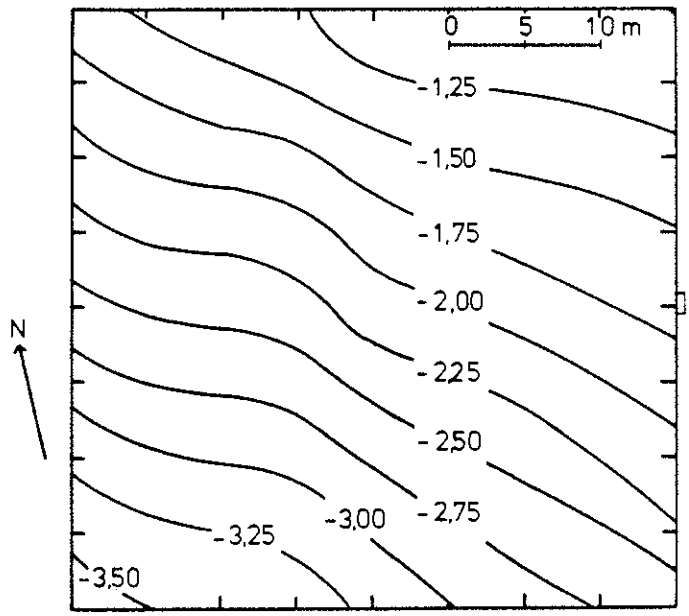

Fig. 2.2. Levelling, North Zealand, beech sample plot. Relative contour lines to the soil surface of the NE-limit of the Norway spruce plot. The difference between the contour lines is 0.25 m. On the right the position of the reopened soil pit is shown. All the pits were dug in the wooded marginal zone.

In the beech and the Norway spruce stands a levelling was taken in 1987. The contour was relatively uniform in the Norway spruce stand, but in the beech stand the difference in level is up to 2.75 m, see Fig. 2.2.

The following provenances were used:
- Norway spruce : Picea abies (L.) Karsten, Rye Nørskov F. 300.
- Beech: Fagus sylvatica L. Lundsgård F. 128a.

Provenance names are according to /6/.

The stands have been thinned in 1983 and 1986 and at each occasion mensurational characteristics of the remaining crop and thinnings were taken, see Tabel 2.1. The thinning in the beech stands was postponed until after litter fall hereby minimizing the influence on the litter sampling programme.

2.2. Sampling programme.

This project has made use of the samples collected within the framework of the main programme. In special cases it has been necessary to install special samplers or to sample in a slightly different way using the same equipment or type of equipment. Within the main programme soil samples have been taken from 8 soil pits excavated in the North Zealand test area. Samples were taken from these pits in such a way that a total of 7 soil profiles have been described and sampled from the beech stand and 6 from the Norway spruce stand. The profile description followed Soil Taxonomy in a Danish modification /7/ and is given in detail in /8/. The soil description and sampling programme has been carried out to a depth of 1.20 m.

Tabel 2.1. Mensurational characteristics, Autumn 1986. Department of Forest Yield, Danish Forest Research Institute

District		North Zealand Frederiksborg		Western Jutland Ulborg	
Tree species		Norway spruce	Beech	Norway spruce	Beech
Age from seed		26	26	26	26
Remaining crop					
Stem number	no./ha	1802	2133	2814	3696
Height	m	12.3	9.7	7.7	6.4
Diameter	cm	13.3	9.6	9.0	6.6
Basal area	m^2/ha	25.1	15.6	17.8	12.5
Volume*	m^3/ha	163.7	118.3	80.6	56.4
Thinning					
Stem number	no./ha	777	1788	370	532
Height	m	12.2	9.0	7.3	6.8
Diameter	cm	12.0	7.7	8.1	6.3
Basal area	m^2/ha	8.7	8.4	1.9	1.7
Volume*	m^3/ha	57.4	53.7	8.4	8.8
Average annual increment from cultivation, 22 years					
Basal area	m^2/ha	2.2	1.3	1.3	1.0
Volume*	m^3/ha	12.7	8.7	5.4	4.3
Annual increment					
Increment period		S.1983-A.86	A.1984-A.86	A.1983-A.86	A.1983-A.86
Basal area	m^2/ha	3.1	2.4	2.1	1.6
Volume*	m^3/ha	27.1	22.7	12.5	8.9

* Beech, total volume

2.2.1. The soil system

The number of roots which could be seen protruding from the pit walls was counted using a 12 x 12 cm plastic net layed out on the wall. The roots were divided into four size clases, 0-2, 2-5, 5-10 and larger than 10 mm in diameter.

Soil samples of size 100 cm^3 have been taken from each horizon in a number of three or a multiple of three for physical analysis. For chemical analysis two composite samples were taken from each horizon, one from each half wall. A composite sample is made up of five 100 cm^3 subsamples.

One soil pit was reopened in 1987 in the beech plot and additional samples were taken to obtain supplementary soil data needed for the ECCES-model calculations, see also Section 3.4. The reopened soil pit was the best choice if only one pit should represent the soil in the whole test area.

Soil water is sampled with the aid of tension lysimeters. The lysimeters are fitted with a porous cup, P-80 material. Possible interferences from this sampling device are described below and in /9/. In /10,11/ test results are also given for a slightly different sampling system which was considered in the first stage of the main programme. Twenty lysimeters were installed in each plot in 1985/86. Then at 40 cm depth, i.e. below the old plough layer, and ten at 90 cm depth. From the root counting it was estimated that 95 % of the roots in both the Norway spruce and the beech plot were situated above 90 cm depth. Water leaching from the 90 cm level is taken to be identical with the water leaching from the ecosystem. Additional lysimeters were installed in the course of the main project, the end result was 13 lysimeters at 90 cm depth in the beech plot and 15 (90 cm-lysimeters) in the Norway spruce plot.

Soil water is taken once a month, in other words the lysimeters are not evacuated continuously. Differences between continuous and discontinuous evacuation are discussed in /9/. The chemical analyses follows /12/ and includes: Ca, Mg, Na, K, Fe, Mn, Al, NH_4, NO_3, Cl, SO_4, PO_4, pH and conductivity. In the context of the present programme analyses for the following trace metals have been carried out: V, Ni, Cu, Zn, Mo, Cd, Sn, Hg, Pb, U and As. The 10 ml soil water sub-samples which had to be analyzed for trace metals were preserved with 0. 1 ml 1 N ultra pure HNO_3 immediately after sampling. These additional measurements were made by ICP-MS (Inductive Coupled Plasma Mass Spectrometry) using the VG-Plasma-Quad instrument at Risø. Only Cu, Zn, Cd (and Al) were analysed for in all the samples.

Three tensiometers were installed to a depth of 40 cm and to a depth of 90 cm in each plot in 1985. The tensiometers are of the type: Soilmoisture Equipment Corporation, Santa Barbara, USA, model 2710. The measurements with the tensiometers are used to estimate the length of the leaching period, or more properly the time interval in which the soil is at field capacity. A soil is said to have reached field capacity if its water content is so high that a little surplus of water will lead to drainage of this surplus. The total volume of water which reaches the ground as throughfall plus stemflow in a period where the soil is at field-capacity is equal to the potential leaching volume.

2.2.2. Litterfall.

The 22 litter traps are mounted diagonally in each plot. The traps are made out of bags of cheesecloth, with opening diameter 53 cm in the beech and 31 cm in the Norway spruce plantation areas. They are mounted on wood racks. Two of the traps in each plot were specially designed to avoid contamination with trace metals. They have the same dimensions as the others. The twenty ordinary traps in each plot were installed in 1985, but the two special ones have only been in function from 1/9-1988 to 1/9-1989. The traps are emptied once a month.

The litter material is sorted into two fractions : leaf litter and a rest fraction. The samples are dried at 60°C, grounded and dry ashed by ignition at 450°C, see /12/. All samples are analyzed for Ca, Mg, Na, K, Fe, Mn, Al, N, P and S. The material from the trace metal traps were dried at 60°C. A 0.5 g sample were placed in a teflon container with 5 ml 4 N HNO_3 and 1 ml 50 % H_2O_2. The container was heated to 140°C for 20 hours in an autoclave. After cooling the clear solution was diluted to 20 ml with water. All reagents are of highest purity. The solutions were analyzed for V, Cu, Zn, As, Cd and Pb by ICP-MS.

2.2.3. Deposition from the atmosphere.

Atmospheric input to the forest is determined as the sum of wet input (rainfall) and dry input (gas and aerosol sampling). Details on sampling equipment and methods are given in /8,9 and 2/.

Bulk precipitation: Sampling is carried out from a tower, 8 m above ground level (2 NILU-samplers) and from 1 m height (2 samplers) and from 2 m height (1 sampler).

Gasses and aerosols: Inlets to the high-volume sampler are mounted at 8 m height above ground level. The gasses SO_2, NH_3 and HNO_3 are sampled on impregnated filters, aerosols are sampled on a front filter. The filters are arranged in a filter package, flow 57 m^3/24 hr. NO_2-sampling is carried out by separate equipment using a modified TGS-method.

Throughfall is sampled by 6 Nilu-samplers (sampling area 314 cm^2) including 2 acid washed systems for samples intended for trace metal analysis. Nitric acid was added to the bottles for trace metal sampling. Throughfall samples are send to the DMU laboratory every half month and analyzed for Na, Mg, K, Ca, Mn, Fe, Ni, Cu, Zn, Cd, Pb.

Stemflow collectors in the form of spirals are mounted on 2 trees of mean diameter in each plot. Stemflow is analyzed for Na, Mg, K, Ca, Mn.

2.3 Soil characteristics

2.3.1. Texture

The grain size distribution gives information on the content of clay, silt, fine sand and coarse sand in the soil. It is common practice in Denmark to use the scheme recognized by the International Society of Soil Science, /13/ : Clay < 2 μm, Silt 2-20 μm, Fine Sand 20-200 μm, Coarse Sand 200-2000 μm. A detail description of soil texture is given in /9/. In this context only results from the soil pit selected for further characterization are reported, see Table 2.2.

The clay content and pH is increasing with depth. In /9/ the correlations are found to be significant. The results from the selected pit are near the test area mean. The profile in this pit has relative uniform horizons which are assumed to be an advantage when only one profile is taken into consideration. An investigation on clay movement was carried out. A distinct argillic horizon could not be detected with the ratio method used.

Table 2.2. Physical properties for soil from the selected soil pit.

Horison	Mean depth cm	Soil colour*	Texture analysis				Volumen-weight	pH		
			Clay 0-2 µm	Silt 2-20 µm	Fine sand 20-200 µm	Coarse sand 0.2-2 mm	g/100 cm^3	H_2O	0.01 M $CaCl_2$	1 M KCl
Ap	0 -25.7	7.5 YR 4.4	14.5	18.6	60.9	6.0	155.20	5.38	4.62	4.43
A_1	25.7-36.9	10 YR 6.4	15.6	25.1	49.2	10.1	166.80	5.85	4.98	4.59
B_{1g}	36.9-57.7	7.5 YR 6.6	20.1	23.8	50.0	6.1	170.85	5.86	4.97	4.47
B_{2g}	57.7-	7.5 YR 5.6	24.7	25.2	46.2	3.9	168.35	5.99	5.03	4.40

* Soil colour, describtion follows Munsell Soil Color Charts.

2.3.2. Pore size distribution.

The maximal water-capacity available to plants is defined as the difference between the soil water content at field capacity (0.1 bar) and the permanent wilting point (15 bar). Methods for determination are described in /12/.

The pore size distribution in the selected soil pit is depicted in Fig. 2.3. The area in the figure covering pores with equivalence diameter 0.2- 30 μm is equal to the maximal plant-available water capacity. The upper layers with a higher content of organic material have a high capacity. Pores in the equivalence class <0. 2 μm are related to the clay-fraction and make up an increasing part of the total pore volume with increasing depth. Large pores (>30 μm) play only a minor part in the profile, because the sand content is low. The pore size distribution as well as the textural findings lies within the normal range in Danish morainic soils as described in /14/.

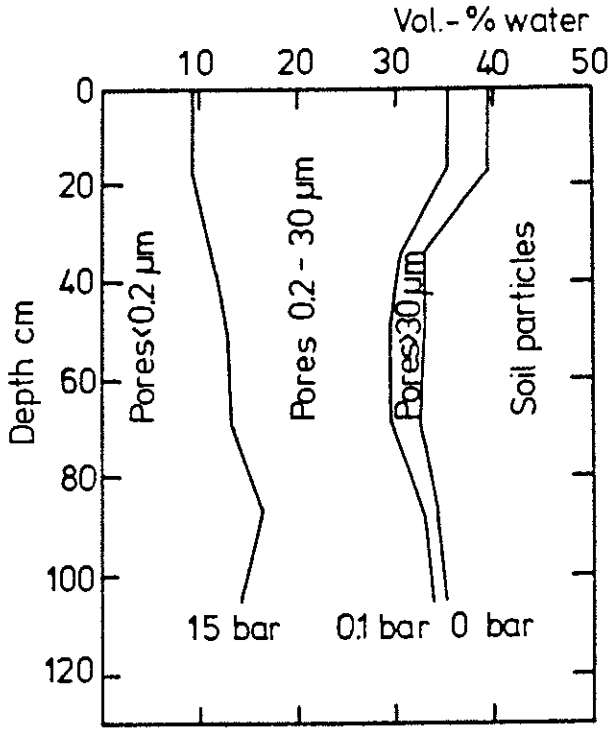

Fig. 2.3. Pore size distribution, North Zealand, soil samples from the reopened soil pit. The area delimitated by the 15 bar line represents the nonplant-accessible amount of water. The area between the 15 bar and the 0.1 bar lines represents the plant-available water capacity. The area between the 0.1 and 0 bar lines represents the minimum air capacity provided the water table lies at least 1 m beneath the relevant depth.

There were no significant differences in plant-available water capacity between the two plots in the test area. The test area means are:

0-90 cm depth: 172 mm
0-70 cm depth: 140 mm
0-40 cm depth: 86 mm

3. SELECTED RESULTS FROM THE SITE INVESTIGATION

3.1. Wet and dry deposition and throughfall.

Atmospheric dry input to the forest canopy are derived from measurement of particle concentrations in the above canopy atmosphere. Mean atmospheric particle concentrations were multiplied with estimated average deposition velocities for aerosols /9/. Deposition velocities are controlled by meteorological and vegetation-specific parameters as well as topography. These parameters are not determined in this project, consequently the dry deposition rates are rough estimates.

Table 3.1. Atmospheric input calculated as bulk precipitation and aerosol deposition for the period 1/1-1989 to 31/12 1989.

	Zn	Cd	Cu	Pb	As
Average element conc. in air* $ng \cdot m^{-3}$	41	0.66***	2.7	31	4.7
Computed dry deposition** (DD) $g \cdot h^{-1} \cdot yr^{-1}$	26	0.41	1.7	19.5	3.0
Measured bulk deposition (BD) $g \cdot h^{-1} \cdot yr^{-1}$	130	0.68	9.7	34.6	3.4
Total atmospheric deposition TA = DD + BD $g \cdot h^{-1} \cdot yr^{-1}$	156	1.09	11.4	54.1	6.4

* Sampling period 1/7-1988 - 30/6-1989
** Dry deposition velocity Vd = $2 \cdot 10^{-3}$ $m \cdot s^{-1}$
*** Estimated from Cd/Zn = 0.016

Results for computed dry deposition and measured wet deposition are compiled in Table 3.1. Dry deposition is calculated using $2 \cdot 10^{-3}$ $m \cdot s^{-1}$ as average deposition velocity.

Wet deposition input is calculated from element concentrations in monthly rainwater samples (bulk samples) multiplied with the precipitation amount collected in the sampling period.

Bulk precipitation is rain sampled in a funnel. The funnel will also sample some dustfall in dry periods. In the Nordic countries the influence of dustfall on the bulk sample concentrations is less than 10 % when focussing on heavy metals. Consequently bulk precipitation gives reasonable estimates for wet deposition. The values obtained in this experiment are in accordance with measurements from earlier years /15/.

Throughfall samples under the canopy contain wet- and dry deposition material from the atmosphere, but it also includes some fine particulated or dissolved biological material originating from twigs and leaves. Samples contaminated with insects and bird droppings are excluded from the computations when identified. Throughfall values for some trace metals are shown in Table 3.2.

Table 3.2. Input to the forest floor as throughfall and stemflow. Frederiksborg 1989. $g \cdot ha^{-1} \cdot yr^{-1}$

	Water	Zn	Cd	Cu	Pb	As
Beech						
Throughfall	$4.69\ 10^9$	141	0.96	10.0	24.8	3.7
Stemflow*	$1.08\ 10^9$	32	0.22	2.3	5.7	0.9
Sum	$5.77\ 10^9$	173	1.18	12.3	30.5	4.8
Norway spruce						
Throughfall	$3.68\ 10^9$	194	1.10	11.6	26.0	5.0
Stemflow*	$0.03\ 10^9$	2	0.01	0.1	0.2	0.1
Sum	$3.71\ 10^9$	196	1.11	11.7	26.2	5.1

* Stemflow fluxes calculated from measured stemflow water flux multiplied with the metal concentrations found in the throughfall water.

It is belived that throughfall values for some elements are close to the total atmospheric input values. This is the case for components such as SO_4^{2-}, Cl^-, Na^+.

Elements such as K, Ca and Mg are recycled through root uptake, leading to higher values for throughfall compared to atmospheric input. This may also be the case for Zn and Cd, elements known to be relatively mobile in plant tissue and soil. Pb is known to be immobile in plants and Pb is also fixed very hard to biogenic material including bark and epiphytes on threes.

The throughfall fluxes of Zn, Cd and Cu are shown to be close to the atmospheric inputs, see Table 3.3, implying throughfall fluxes of these elements to originate from atmospheric dry and wet deposition. The contributions from litterfall to the total fluxex to the forest floor are discussed in Section 3.2.

Table 3.3. Trace metal fluxes to the forest canopy and to the forest floor. Frederiksborg 1989. $g \cdot ha^{-1} \cdot yr^{-1}$

	Zn	Cd	Cu	Pb	As
Total atmospheric deposition	156	1.1	11.4	54.1	6.4
Beech					
Throughfall + stemflow (TS)	173	1.2	12.3	30.5	4.8
Litterfall* (L)	474	1.3	26.6	24.8	1.1
TS + L	647	2.5	38.9	55.3	5.9
Norway spruce					
Throughfall + stemflow (TS)	196	1.1	11.7	26.2	5.1
Litterfall* (L)	392	1.3	14.8	15.6	0.9
TS + L	588	2.4	26.5	41.8	6.0

* Litter results from Table 3.5 including estimated contribution for May month.

The throughfall of Pb is somewhat smaller than the atmospheric input in the same period. It is known from other investigations /16,17/ that only a few percent of the Pb content in plants has been taken up by the roots. The major part - 90-97 % - of the Pb found in the above-ground parts of plants originates from atmospheric deposition directly to the plant surfaces. This is probably also the case for trees. Low throughfall fluxes of Pb compared to atmospheric input are the result of absorption of atmospheric lead to the plant surfaces.

In case of As the patern seems to be similar to Pb. However, the present knowledge about the behaviour of As is much more limited and conclusions are not possible at this stage.

3.2 Litterfall.

The litter sampling periods in the main programme run from April to April. In the trace metal investigation it has not been possible to use the same sampling period, instead the period runs from 1/9-1988 to 1/9-1989.

Dry weight figures from the beech and Norway spruce stands can be seen in Table 3.4. The year to year variation in the total flux of litter is about ± 20 percent. In 1988/89 the amount of beech litter was the heighest in the four-year period. In contrast the spruce litter was below the four-year mean value.

Table 3.4. Annual litterfall in the period 1/4 1985 - 1/4 1989 for the beech and Norway spruce stands. ton dry weight·ha^{-1}·y^{-1}

Frederiksborg North Zealand		85/86	86/87	87/88	88/89
Beech	Leaves	2.8	2.6	2.4	3.2
	Rest	0.9	0.7	0.7	1.1
	Total	3.7	3.3	3.1	4.3
N. Spruce	Needles	3.5	2.4	1.8	2.0
	Rest	0.3	0.3	0.3	0.3
	Total	3.8	2.7	2.1	2.3

Fig. 3.1. Monthly litterfall in ton·ha^{-1}. Litter from June, July and August which was not sorted out in fractions is shown cross hatched. Black: Leaf or needle litter. White : Other materials.

The amount of litter varies from year to year due to climatic and biological reasons. In years with a mild climate like the preceeding ones, especially the mild winters, the possibility for a build-up of needle year classes is present resulting in lower amounts of needle litter for this year.

The amounts of litter trapped by the two trace metal traps and the twenty ordinary traps in each plot has been compared. The hypothesis that trace metal traps have collected true subsamples of litter could not be rejected by means of a Student t-test on a 5% level. No statistical difference has been found between the twenty ordinary traps from the main programme and the trace metal traps in neither of the two litter fractions, leaves or needles and the rest fraction (litter per trap/month). The estimated litterfall based on the twenty traps has therefore been used in the calculation of the fluxes in Tables 3.5. and 3.6. and Figs. 3.2. and 3.3.

The dry-weight figures in Table 3.5. are not identical with the figures in Table 3.4. for the year 88/89 due to the different sampling periods.

The total flux of Pb and Cu is much higher in the beech stand than in the spruce stand, see Table 3.5.

Trace metal figures for leaf- and needle-litter have not been available up to this point for Danish materials, but it is known from an investigation /18/ of trace metal concentrations in moss samples, that markedly regional differences exist in the trace metal deposition in Denmark, see Table 3.6.

Table 3.5. Total flux of trace metals with litter in the period 1/9 1988 - 1/9 1990. (The samples from May were not analysed and the contribution to the total flux is not included).
$g \cdot ha^{-1} \cdot y^{-1}$

Dry weight	Zn	Cd	Cu	Pb	V	As
	Frederiksborg Beech					
$4.14 \cdot 10^6$	433	1.18	25.01	23.06	3.56	1.04
	Fredriksborg Norway spruce					
$2.98 \cdot 10^6$	346	1.07	11.9	12.6	2.55	0.766

Table 3.6. Trace metal concentrations in leaf litter and in the moss Pleurozium Schreberi (Brid) Mitt. in North Zealand. Moss figures from /18/. Figures in brackets are median values. Concentrations in leaf litter are weighted means for the period 1/9 1988 - 1/9-1989, (results for May 1989 missing). $mg \cdot kg^{-1}$

Zn	Cd	Cu	Pb	V	As
Frederiksborg Beech					
71.9	0.25	4.9	3.7	0.56	0.18
Frederiksborg Norway spruce					
108.1	0.35	3.3	3.2	0.54	0.16
North Zealand moss-samples					
60-80	0.30-0.50	18.0-12.0	40-60	>12.0	0.40-0.80
Mean Denmark moss-samples					
56 (52)	0.43 (0.39)	9.7 (8.6)	33 (31)	11.3 (9.6)	0.71 (0.64)

Care must be taken to compare metal concentrations in litter and moss because moss has no real roots but often rhizoids. In /2/ very low trace metal concentrations from soil water in and below the root zone are reported, except for Cu. Nevertheless some trace metals could be taken up by the trees from the topmost part of the soil. It is known that especially Zn- and Cd-ions are readily taken up by the tree roots. These metals can be recycled to the soil, either leached from the needles or returned as litterfall. A certain amount can be incorporated into biomass and thus temporarily be removed from internal cycling /20/.

Moss samples collected in the North-Zealand area have a Cd and Zn content which is comparable to the measured concentrations in the litter, in contrast the concentrations of Cu, Pb, V and As are lower in the litter. From the difference in trace metal concentrations in moss between the North Zealand figures and the Denmark mean figures, one could expect the North Zealand litter samples to be in the high end. On this basis it is not possible to assume the trace metal concentrations in the litter samples from North Zealand to be representative for Denmark as a whole. Above-mean figures could be expected in the litter for Zn, Pb and V, judged from the moss samples.

In /18/ two trace metal groups were identified by means of a principal component analysis. One group contains As, V and perhaps Pb, another group contains Cd, Zn and perhaps Cu and Pb. The former group derives from anthropogenic (industry, power-plants, waste disposal industries) and natural sources (dust and aerosols), the latter

Table 3.7. Mean annual flux of trace metals with litter in different Central and North European ecosystems. $g \cdot ha^{-1} \cdot yr^{-1}$

Element	Denmark	Sweden			F.R.G.					
	* Frederiks-borg	21 Gårdsjön	21 Värsjö	20 Bergkvist	22,23 Wingst	22,23 Harste	22,23 Spanbeck	24 Black Forest	25 Solling	22,23 Solling
Beech										
Zn	474	-	-	59-200	-	112/78	-	50-160	260	185/170
Cd	1.32	-	-	0.35-1.2	-	0.84/0.8	-	0.5-1.2	2.6	1.38/1.3
Cu	26.6	-	-	1.8-3.4	-	21.6/13	-	10-26	75	45.2/33
Pb	24.8	-	-	18-38	-	34/34	-	16-34	120	81/61
Norway spruce										
Zn	392	230	210	110-210	168/118	-	95/75	50-160	250	112/109
cd	1.25	0.5	0.7	0.32-1.2	1.06/0.8	-	0.89	0.5-1.2	2.3	1.1/1.1
Cu	14.8	12	17	12-19	40.5/10	-	15.1/11	10-26	240	23.3/22
Pb	15.6	9	74	52-83	118/57	-	50/44	16-34	256	147/116

* Present investigation. Results for May 1989 estimated.

/21/ 1980-84, 3 yr.
/21/ 1980-81, 2 yr.
/20/ 1984-87, 3 yr.
/22/ 1983-85, 2 yr.
/23/ 1983-84.
/24/ 1982-84, 2 yr.
/25/ 1973-77, 4 yr.

/26/ from 1988, gives figures for Pb in litter for three Danish stands of Norway spruce:

Klosterhede: 72 $g \cdot ha^{-1} \cdot yr^{-1}$
Tange: 58 $g \cdot ha^{-1} \cdot yr^{-1}$
Strødam: 95 $g \cdot ha^{-1} \cdot yr^{-1}$

derives mainly from anthropogenic emission sources. The maps in /18/ indicate that the group containing Cd and Zn is the prevailing group in North Zealand. So far a principal component analysis has not been carried out on litter data.

The monthly fluxes are indicated on Figs. 3.2. and 3.3. A comparison between the ton/ha distribution and the Zn, Cd distributions for Norway spruce reveals almost the same distribution and furthermore that the main part of the flux is with the needle litter. A different distribution shows up for V and As and here the flux of trace metals is more pronounced in the fraction "other materials". It looks like the presented distributions reflect a two factor grouping.

The monthly fluxes of trace metals in the beech stand reflect closely the litterfall in the autumn, see Fig. 3.3. One comment is necessary on the mean flux of Zn in November in beech, the mean flux is made up of two very different figures.

The flux of trace metals in temperal forest ecosystems has recently been reviewed /20/. and litterfall was found to be important for the flux of Zn for some deciduous trees. In some relatively unpolluted areas of Europe, like the Black Forest, a relative large part of the total Pb flux is also transported by litter. The authors conclude that the flux of trace metals with litter relative to throughfall is more important in unpolluted areas compared to polluted.

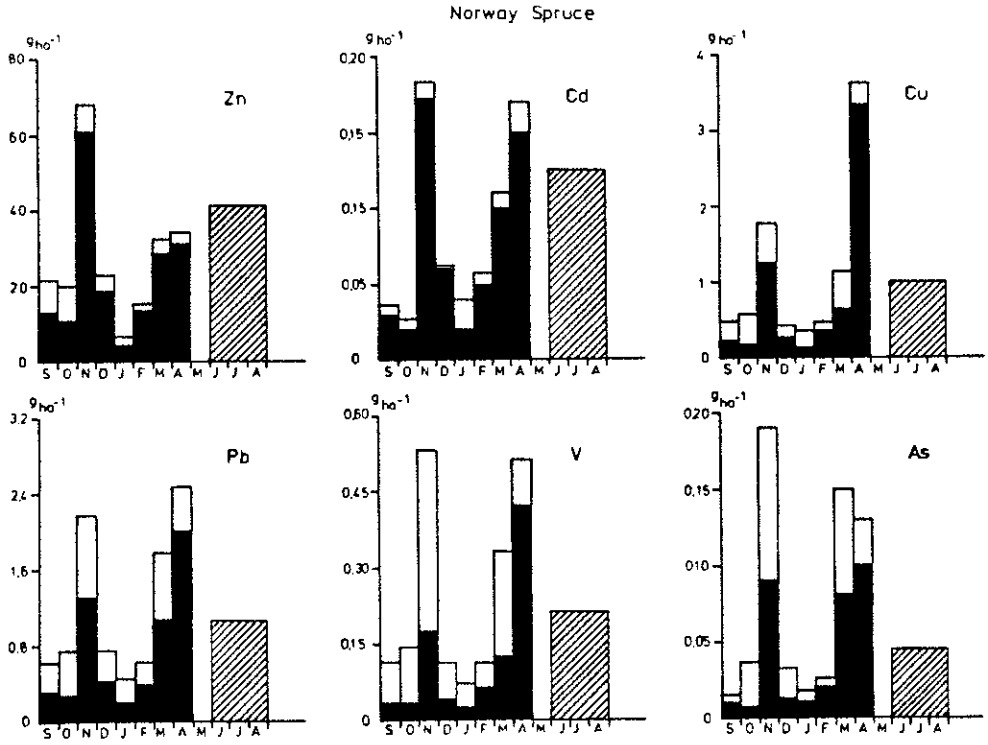

Fig. 3.2. Norway spruce. Frederiksborg, North Zealand. Monthly flux of trace metals with litter. Litter from June, July and August which was not sorted out in fractions is shown cross hatched. Black: needle litter. White: Other materials. Results from May excluded.

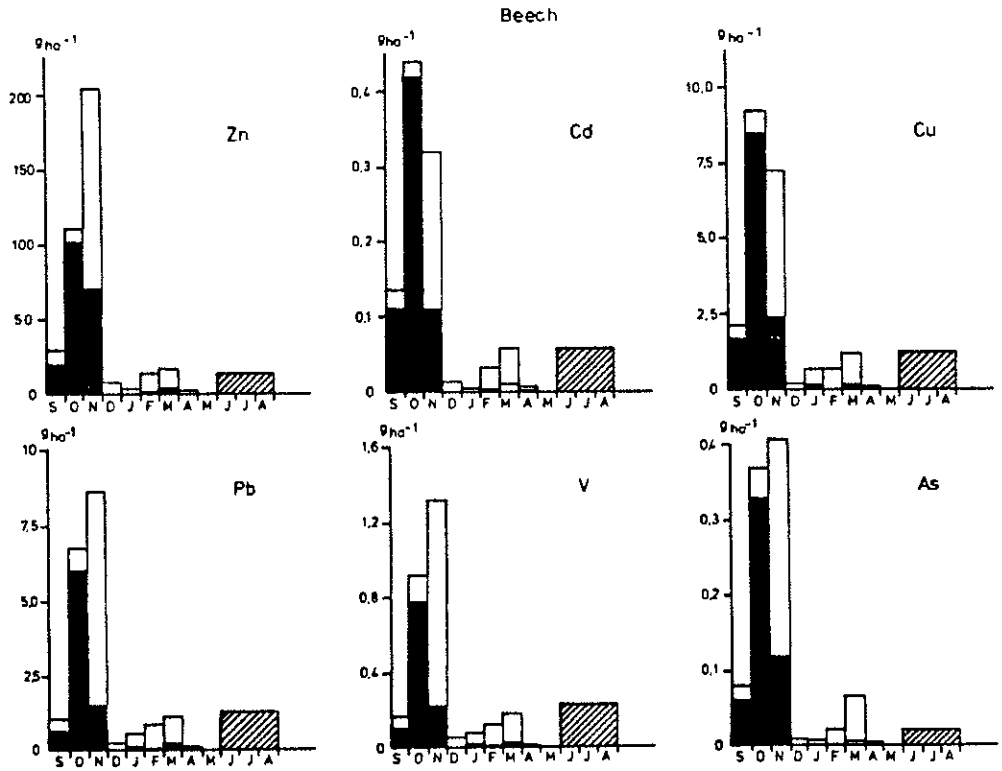

Fig. 3.3. Beech. Frederiksborg, North Zealand. Monthly flux of trace metals with litter. Litter from June, July and August which was not sorted out in fractions is shown cross hatched. Black: Leaf litter. White: Other materials. Results from May excluded.

Some values for litter flux taken from the literature are given in Table 3.7. and compared with the values from this investigation. The flux in Norway spruce of Cd, Cu and Pb is comparable to the fluxes reported e.g. from Sweden, but the flux of Zn is even higher than the flux in the Norway spruce stand (F1) in Solling.

The fluxes in the beech stand, Frederiksborg, are generally of the same magnitude as the flux-figures from Central Europe, but as for spruce the flux of Zn in the beech stand is also very high, compared to the other stations. It should, however, be kept in mind, that the litterfall in 1988/89 was the highest recorded in the four-year investigation period.

The total fluxes of trace metals to the forest floor are given in Table 3.3. together with the throughfall plus stemflow fluxes and the flux with litterfall. In conjunction with /27/ it is concluded that the input of Zn and Cd to the soil surface is to a large extend part of the internal cycling of these elements. It seems, from the data obtained in the present study, that the internal cycling for Cu is equally important. It should be pointed out, that despite stemflow only contributes a fraction of the water reaching the ground, it is characterized by high concentrations of trace metals, and especially so in conifers /20/. The stemflow fluxes, Tables 3.2. and 3.3. are therefore especially for spruce underestimated, see footnotes to the tables. Judged from data from Southern Sweden /20/ the stemflow fluxes in spruce are 5-10 % of that in throughfall.

It is well known that lead is often trapped by canopies so that throughfall in relatively unpolluted areas contributes a lower Pb flux than bulk precipitation, see Tables 3.1. and 3.2. In this study it appears that the sum of throughfall, stemflow and litterfall of Pb (and As) agrees with the atmospheric input to the forest, see Table 3.3.

3.3. Soil water composition.

Interference properties of the tension lysimeter soil water samplers on sampled trace metal concentrations, have been investigated as reported in /2/.

Two laboratory experiments were conducted: One with suction of a 100 ppb Cd-solution followed by a 50 ppb and lastly by a 100 ppb-solution through new unused lysimeters. The other experiment was a sorption/desorption experiment with radioactive tracers ^{63}Zn and ^{115m}Cd in two concentrations: 3.9 ppb resp. 39 ppb Zn and 3.5 ppb resp. 42 ppb Cd in 10^{-3} M $CaCl_2$. The experiments showed clearly no sorption of Cd on the lysimeters, but sufficient suction solution, about 100 ml, should be used to reach 100 % recovery. The experimental part with Zn showed sorption phenomena, ~ 50 % negative interference. However, it was concluded that in the long run, when the cup has been used for an extended period of time, the Zn-effect is presumably small and will tend to narrow the variation in the measured Zn-concentrations and perhaps other element concentrations.

The analytical difficulties encountered when using the then quite new ICP-MS technic for trace element analysis of soil water samples are discussed in /2/. The inital problems have been overcome and the instrument is now in routine use. However, with solutions containing considerable quantities of other salts as is the case here, considerable effort is required to obtain reliable results in the < 5 ppb concentration range. A detection limit of 0.2 ppb were achieved for Cd but was in many cases still insufficient.

With reservations, typical concentrations for soil water samples obtained at 90 cm depth in the sampling period 1/12 1987-1/5 1988 were:

Zn: 10-20 μg/l
Pb: < 5 -
Cd: < 0.5 -

No obvious variation with sampling month can be seen. In case of Zn there is a tendency to about a factor 2 higher concentrations in water from the 40 cm lysimeters.

The analyses for Cu are also discussed in /2/, but the variation is too wide for conclusion to be drawn. Some typical analyses for other elements are V: ~1-10 μg/l and U: <0.5 μg/l, but these elements were not analysed in all the samples.

In a recent review /20/ figures from temperate forests are stated. In comparison the here measured Cd- and Pb-concentrations are in the low or very low end.

However, at least the Cd concentrations are in good agreement with the contents and the distribution coefficients determined for the elements in these clayey soil samples, see Section 3.4.3. (Fig. 3.5. yields for example a Cd concentration of ~1 ppb in 0.001 M $CaCl_2$ solution in contact with soil with 0.2 ppm Cd. The agreement for Zn is less good: Fig. 3.7. indicates that a soil with 59 ppm Zn should yield a solution with about 600 ppb Zn in 0.001 M $CaCl_2$, i.e. about a factor 30-50 higher than what is actually the case. This is probably due to the tendency to slow desorption of Zn from the soil as it is also illustrated by Figs. 3.7-11.)

This and the general lack of detail in the analytical results for heavy metals in soil water makes a comparison with calculation results from the ECCES soil model rather uninteresting. The model validation in Section 4 has therefore been limited to the pH and the macro-ions, primarily Ca.

It could be hazardous to calculate the flux of heavy metals out of the rootzone from figures representing only a limited period, few samples, wide variations in the measured concentrations and measurements often near the detection limit. But attention is drawn to the Zn figures bearing the high Zn-concentrations in litter in mind. To give an impression of the level the Zn-fluxes are tabulated together with values from the literature in Table 3.8.

Clearly the Zn-flux estimated from this investigation is in the low end. The explanation for the low flux out of this formation compared with the others is probably the clayey soil type.

Table 3.8. Trace metal flux out of the rhizosphere. All figures are from Norway spruce. $g \cdot ha^{-1} \cdot yr^{-1}$

Element	Denmark				Sweden			F.R.G.		
	* Frederiksborg	26 Kloster-hede	26 Tange	26 Strødam	21 Gårdsjön	21 Värsjö	20 Bergkvist	22 Wingst	22 Spanbeck	25/22 Solling
Zn	15 - 60	290 - 460	20 - 220	790	456	560	650- 1300	527	350	2364/1573

* Present investigation, rough estimate.
Sampling period: 1/12 1987 - 1/5 1988. Tension lysimeter data, P 80 cup.
/26/ 1983/84 - 87, 1 - 4 years. Tension lysimeter data, P 80 cup.
/20,21/ Zero tension lysimeter data.
/22,25/ Tension lysimeter data, P 80 cup.

The soil water composition for the elements measured in the main programme is reported elsewhere /9,19,3/. Mean soil water concentrations are, however, listed in Table 4.9. for comparison with the model calculations. It should be noted that the outflux figures from the beech plot in North Zealand has been recalculated on the basis of the following findings from the low level part. The findings summarized here have been reported earlier in /8,9,2/, except no. 7 and 8:

1. The contours delimitate the SW part of the plot.

2. The profiles described from this low end are complex in nature - horizons with a high sand contents shift over to horizons with a high clay content, the latter with structural bands.

3. Microvariations have been found in the textural composition - described by the ratio method.

4. The pore size distribution is abnormal in this part of the plot in 70-90 cm depth. This finding is closely correlated with 2).

5. Results from observation wells and piezometers in this part of the plot, and only in this part have revealed the presence of at least three separate water tables in 2, 3 and 4m depth, the curves run parallel through the year indicating impeded water.

6. For a short period in the winter 1985/86 the water table measured in the observation well reached the maximum registered height in the four years of measurement 1 m below ground level.

Recalling the definition of field capacity and the presence of a capillary fringe zone there must be a maximum distance from a sampler to the water table of at least 1 m. The inlet to the tension lysimeter is through the cup mounted to a maximal depth of 90 cm. Taken together this means a distance from ground level to maximal height of the water table of at least 1. 90 m. The relative contour line which fulfils these requirements is the -3.00 m line. This line delimits 12.6 % of the plot and 3 tension lysimeter stations.

7. Infiltrometer investigations, not reported earlier, has shown the infiltration capacity to be influenced by subsoil factors. Readings were taken on four days in succession, each day supplying 100 mm of water, a maximum infiltration rate was found. Relating the maximum rate to mm of water and the level on which the measurement was taken and calculating backwards using the pore size distribution to the lowest part of the plot reveals a position of these soil factors to be in 150-200 cm depth. A finding almost consistent with the position of the impeded water-layers (-2 m) discussed above.

8. Highly significant differences in an analysis of variance were found between the three lysimeter stations delimitated by the -3 m contourline and the rest for the following parameters : Sample size, the concentrations of Ca, Na, K, NO_3, SO_4 and Cl. The statistical analysis enclosed 2 years of data.

In recalculating the outflux data from the beech stand the lowest 12.6 % of the plot area and samples from the three tension lysimeter stations are excluded.

3.4. Soil properties.

The site measurements gives a present day status for a relatively unpolluted area. Simulation of these data using the ECCES soil model requires some information about the soil in addition to those given in Section 2.3.

If the soil chemistry model is to be used in long-term predictions it is also important to investigate how the soil is likely to behave when exposed to more extreme conditions, i.e. larger amounts of acid precipitation.

3.4.1 Sampling of the soil and general properties.

In the autum of 1987 soil samples from horizons between 5-25, 30-45, 55-75 and 90-110 cm were obtained from the selected soil pit in the beech stand, see Fig. 2.2. The samples (some kg each) were mixed, air dried, crushed, sieved through 2 mm nylon net and stored in stoppered glass bottles.

In January 1989 a sample of undisturbed surface soil: the top 0-5 cm layer was also collected from near the same place. The F and H layers were not developed.

Table 3.9. Mean values of two determinations of water contents, oxidizable materials and pH for soil samples from 5 layers in the selected soil pit at the experimental area in Frederiksborg forest district.

Soil sample from layer	Clay	Weight loss 110°C	Weight loss 550°C	COD as CH_2O	pH 2 water/1 soil, centrifuged
	%	%	%	%	
0-5 cm	0.99	4.3	4.3	-	
5-25 cm	14.5	0.87	2.7	1.9	5.44
30-45 cm	15.6	1.35	2.0	0.5	5.88
55-75 cm	20.1	1.36	1.8	0.3	5.97
90-110 cm	24.7	1.46	1.9	0.3	6.00

Clay contents (taken from /9/), remaining water, weight losses on ignition and chemical oxygen demands: COD recalculated as the equivalent amount of CH_2O are given in Table 3.9. The pH was measured in the supernatant from centrifugation of 2 water/1 soil mixtures. See also /2/ for further comments and details.

From the table it is seen that the pH increases slightly down through the profiles. Also the clay content is increased while the amount of organics is decreasing.

3.4.2 Ion exchange capacities.

Ion exchange is the dominating mechanism regulating short-term variations in the water chemistry of most soil types.

The size of the cation exchange capacity: CEC - traditionally given in meq/100 g soil - is important for the buffer capacity of the soil and for the concentration in the pore water of the dominating cations: primarily Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and in acid soil Al^{3+}. For the micro-components the total CEC is of less importance, see Section 3.4.3.

The cation-exchange capacity may conveniently be separated into a permanent (pH independent) and a variable (pH dependent) capacity designated CECP and CECV, respectively. The total capacity $CEC_{8.2}$ = CECP + $CECV_{8.2}$ is determined experimentally using a method based on equilibration with Ba^{2+} ions in triethanol amine buffer at pH 8.2 according to /28/. The permanent capacity is determined in a similar manner but after equilibration in acid solution (pH ~2). Aluminum analyses of the extracts gives the fractions of the capacities covered by Al-ions.

Results for the soil samples investigated here are given in Table 3.10. It is seen that CECP is increasing systematically down through the soil while CECV is decreasing so that the total CEC at pH 8.2 is nearly constant. CECP appears to be correlated with the clay content:

$$\text{CECP (meq/100 g soil)} = 0.33 \cdot a \text{ (\% clay in soil)}$$

CECV is probably determined by a combination of the contents of organics and of various Mn- or Fe-containing minerals. On the background of literature values it is assumed that CECV = 0 for pH<4.

This assumption is used in plotting the CECP and $CEC_{8.2}$ measurements in Fig. 3.4. The figure does also include measurements of the total CEC at pH around 5.4 to 6, i.e. near the actual values found in the soil. Although this is not particularly acid soils it is seen that a considerable part of the CECV capacities are consumed already at this pH

Table 3.10. Mean values of two determinations of CECV, CECP and Al^{3+} or H bound to the ion exchange sites for soil samples from the 4 below surface layers in the selected soil pit at the experimental area in Frederiksborg forest district. The modified CECV values gives the correct total CEC at the actual soil pH using linear interpolation, see text.

Soil sample from layer:	equilibrated at pH 8.2			equilibrated at pH ~2				Modified $CECV_{max}$
	Al^{3+} ion ex.	H	$CEC_{8.2}$	$CECV_{max}$	CECP	Al^{3+} ion ex.	Al^{3+} total in sol.	
	meq/100 g dry soil							
5-25 cm	0.3	6.0	11.1	7.0	4.1	2.8	8.3	2.9
30-45 cm	0.1	4.2	12.1	5.5	6.6	5.0	10.5	2.5
55-75 cm	0	4.0	11.6	4.8	6.8	5.3	11.9	1.0
90-110 cm	0	4.1	12.5	4.6	8.0	8.3	14.4	1.0

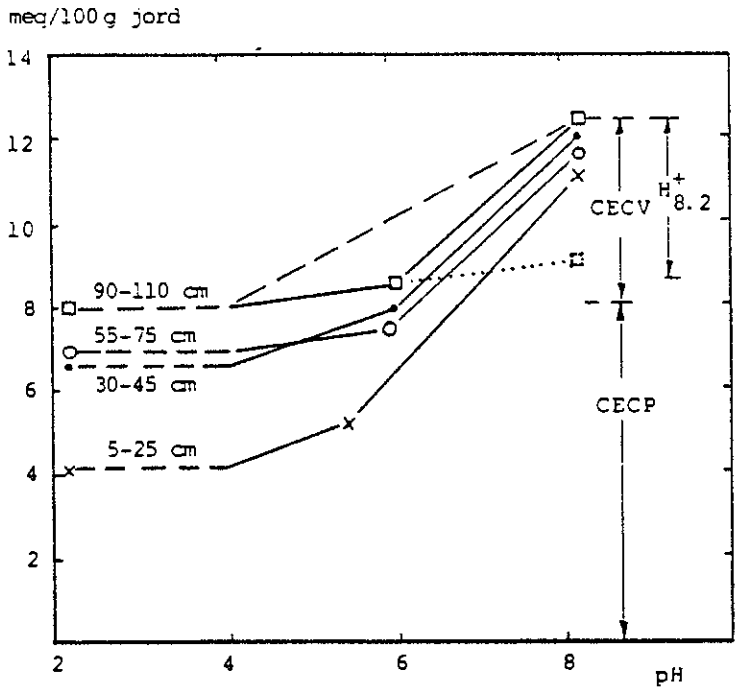

Fig. 3.4. Cation exchange capacities and released H^+ by pH change from ~6 to 8.2 for samples from four soil layers in the selected pit in the Frederiksborg forest district.
The arrows to the left show the CECV, CECP and released H^+ for the bottom layer (90-110 m). The dotted line shows for the same layer the simplified CEC/pH relationship used in the modelling in Section 4.

range. The linear relationship assumed in the ECCES model /29/ between CECV and pH for $4<pH<8.2$ is shown for layer 90-110 cm as a dashed line. The deviation from the measured values is seen to be considerable and the relationship should probably be represented by an S-shaped curve. However, since the values at higher pH is of minor interest for the simulation of the acidification of the soil, it is proposed to retain the linear relationship for the simulations described in Section 4, but use the modified $CECV_{max}$ values given to the right in Table 3.10. This is shown by the dotted line for layer 90-110 cm in Fig. 3.4.

In addition to the cation exchange capacity some soils may also have some anion exchange capability. This has been investigated but only for soil from layer 55-75 cm. ^{32}S tracered SO_4^{2-} solutions were equilibrated with the soil samples at various pH. The method and the results are decribed in /2/. However, the anion exchange capacity was found to be low (< 0.1 meq SO_4^{2-}/100 g soil at pH> 3) and on the margin of what can be measured with the experimental method. It is of no importance for the simulations in Section 4.

3.4.3. Ion exchange equilibria.

Retention of minor components in the soil such as the cations Cd^{2+} and Zn^{2+} may occur by ion exchange in competition primarily with the macro-components, mainly Ca^{2+}. The degree of retention is determined by the equilibrium constant. The variation of this parameter has been investigated experimentally using Ca^{+2} as competing ion. Soil samples from layer 55-75 cm were used in most of the experiments, but the difference in behaviour of soil from the other layers is probably slight.

For ion exchange competition between divalent ions according to:

$$Cd^{2+} + CaX_2 = CdX_2 + Ca^{2+}$$

or

$$Zn^{2+} + CaX_2 = ZnX_2 + Ca^{2+}$$

the mass law expressions are:

$$\frac{[CdX_2] \cdot (Ca^{2+})}{(Cd^{2+}) \cdot [CaX_2]} = K_{Cd/Ca}$$

and

$$\frac{[ZnX_2] \cdot (Ca^{2+})}{(Zn^{2+}) \cdot [CaX_2]} = K_{Zn/Ca}$$

Here $[CaX_2]$ represents the concentration of Ca on the ion exchange sites and (Ca^{2+}) the activity of Ca in solution, etc.

Furthermore, at not too low pH values where the base saturation of the permanent capacity is ~1, it can be assumed that the capacity is completely covered by Ca, Cd and/or Zn:

$$2\cdot([CaX_2] + [CdX_2] + [ZnX_2]) = CEC$$

Rearrangement gives:

$$[CdX_2] = \frac{0.5 \cdot CEC \cdot (Cd^{2+})}{(Ca^{2+})/K_{Cd/Ca} + (Cd^{2+}) + (Zn^{2+})/K_{Cd/Zn}}$$

and

$$[ZnX_2] = \frac{0.5 \cdot CEC \cdot (Zn^{2+})}{(Ca^{2+})/K_{Zn/Ca} + (Zn^{2+}) + (Cd^{2+})/K_{Zn/Cd}}$$

where $K_{Cd/Zn} = K_{Cd/Ca}/K_{Zn/Ca}$, etc. The expressions can easily be extended to comprise additional cations.

Most of the experiments in this investigation were, however, conducted with only Cd or Zn present together with the calcium, and the last term in the nominator is therefore irrelevant. Since all the ions are divalent the activity coefficients are the same and the activities can therefore simply be substituted with the concentrations in the solution. This gives the usual expression for a Langmuir adsorption isoline:

$$[CdX_2] = \frac{0.5 \cdot CEC \cdot [Cd^{2+}]}{[Ca^{2+}]/K_{Cd/Ca} + [Cd^{2+}]}$$

If in addition $[Ca^{2+}]/K_{Cd/Ca} >> [Cd^{2+}]$ the expression is reduced to:

$$[CdX_2] = \frac{0.5 \cdot CEC \cdot K_{Cd/Ca}}{[Ca^{2+}]} \cdot [Cd^{2+}] = K_D \cdot [Cd^{2+}]$$

where K_D is the distribution coefficient normally given in the unit ml/g. It follows that K_D is a function of CEC, K and the concentration of the macro-ion, here Ca^{2+}. To be meaningful the K_D concept also requires that conditions of the type $[Ca^{2+}]/K_{Cd/Ca} >> [Cd^{2+}]$ are fulfilled which may not necessarily be the case even for micro-elements if the K value is high. K_D values taken e.g. from literature should therefore always be regarded with considerable scepticism.

In logarithmic form the expression is:

$$\log[CdX_2] = \log(0.5 \cdot CEC \cdot K_{Cd/Ca}) - \log[Ca^{2+}] + \log[Cd^{2+}]$$

It follows that plotting the concentration of Cd on the ion exchanger versus the concentration in solution on log/log scales should give a series of straight lines with unit slope and with unit distance between the lines when the Ca^{2+} concentration is increased in steps of one decade.

3.4.3.1. Experiments.

Experiments have been conducted to investigate the distribution behaviour of Cd and Zn versus Ca in soil samples from the test area. The soil was in most cases from the 55-75 cm layer.

The radioactive isotopes ^{115m}Cd and ^{65}Zn were used as tracers for Cd or Zn added as chlorides in various amounts to soil samples previously saturated with $CaCl_2$. The amounts adsorbed on the soil were calculated as difference between the added Cd or Zn and the contents found in solution after equilibration and centrifuging. The water-to-soil ratio was in all cases about 10. The equilibration procedure consisted normally in one hour vigorous shaking in centrifuge tubes of polycarbonate (from Nalgene) which were then left standing to the next day before a renewed shaking for one hour. The experimental method is described in details in /2/.

3.4.3.2 The Cd/Ca system.

Fig 3.5. shows the results for cadmium in form of the above mentioned log/log plots of the measured Cd concentrations in soil versus the concentrations in the solutions. Each group of three interconnected points represents the value found after the initial absorption equilibration (the point to the right) followed by two desorption values found after two equilibrations with pure $CaCl_2$ solution.

Three different $CaCl_2$ concentrations were employed. The 10^{-3} M Ca^{2+} solution is the concentration most aking to actual values found in the soil pore water. The ~0.2 ppm Cd found to be normally present in the soil (see Table 3.11.) is indicated by an arrow on the figure. The three lines with slope 1 represents the formula:

$$\log[CdX_2] = \log(0.5 \cdot 0.075 \cdot 1.7) - \log[Ca^{2+}] + \log[Cd^{2+}]$$

where 0.073 meq/g is the total CEC value for this soil at the pH ~6 measured in the equilibration solutions (see Fig. 3.4.)

It is seen that the approximation is not at all good at low Cd concentrations. This could be remediated by displacing the lines to the left corresponding to $K_{Cd/Ca}=6.9$ instead of 1.7. The expression would then give too low solution concentrations at higher Cd contents in the soil and the influence of changes in Ca concentration would still be exaggerated. This is the type of relationship which was originally introduced into the ECCES soil model. In the case of Cd a modified version based on an empirical data has also been implemented taking also pH effects into account, see /30/.

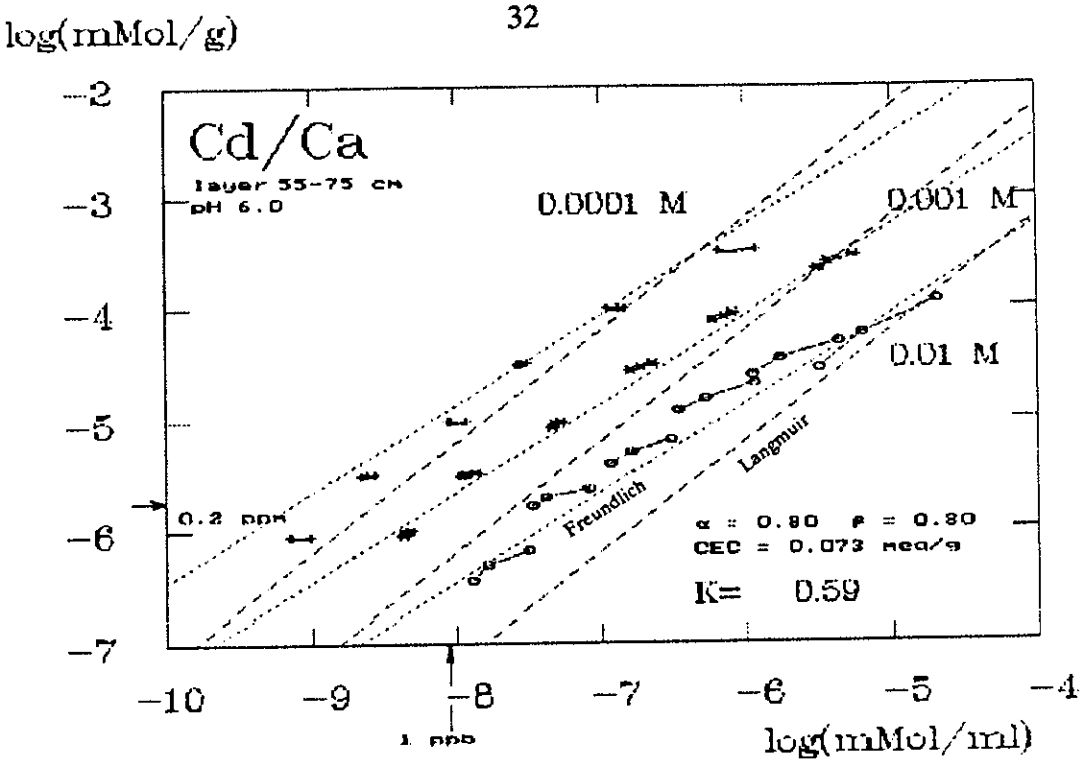

Fig. 3.5. Results from adsorption and desorption experiments using ^{115m}Cd in soil from layer 55-75 cm and addition of different amounts of Cd at three different Ca^{2+} concentrations. Each group of three points represents one adsorption (to the right) and two desorption equilibrations. The stippled lines represents Langmuir approximations while the dotted lines are from a Freundlich expression using parameter values indicated in the bottom left corner of the figure.

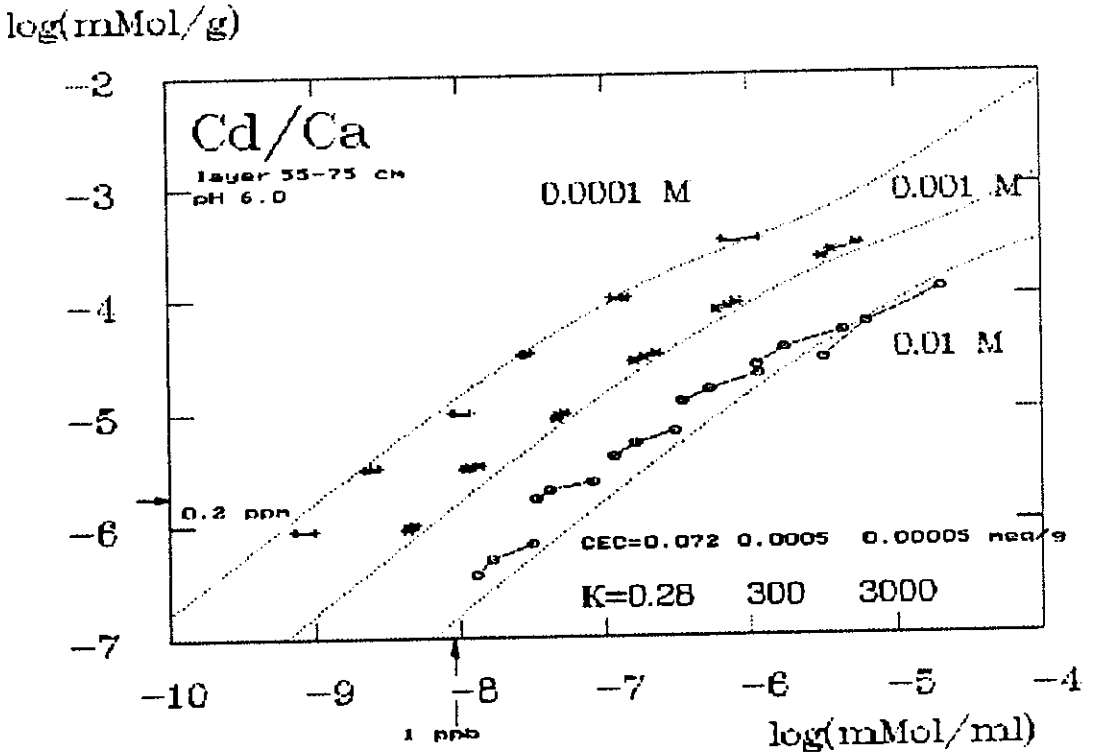

Fig. 3.6. Same results as above but approximated with a "multi-Langmuir" expression using the three set of CEC and K parameters indicated on the figure. The 0.2 ppm indicated on the ordinate is the actual concentration of Cd found in this soil.

An equation of the Freundlich type:

$$\log(CdX_2) = \log(0.5 \cdot 0.075 \cdot 0.53) + 0.8 \log[Cd^{2+}] - 0.8 \log[Ca^{2+}]$$

is seen to give a better approximation to the experimental results in Fig. 3.5. as indicated by the three dotted lines with slope 0.8 and distance 0.8, but the exponents are purely empirical and the straight lines do not reflect the tendency to bending of the curves.

Of more interest for understanding the mechanisms is a representation based on the assumption that the observed results can be interpreted as the combined effect of a number (n) of different types of ion exchange sites each having its own characteristic CEC and $K_{Cd/Zn}$ value. For n=3 the "multi-Langmuir" isoline is then given by:

$$[CdX_2] = \frac{0.5 \cdot CEC1 \cdot [Cd^{2+}]}{[Ca^{2+}]/K1_{Cd/Ca} + [Cd^{2+}]} + \frac{0.5 \cdot CEC2 \cdot [Cd^{2+}]}{[Ca^{2+}]/K2_{Cd/Ca} + [Cd^{2+}]} + \frac{0.5 \cdot CEC3 \cdot [Cd^{2+}]}{[Ca^{2+}]/K3_{Cd/Ca} + [Cd^{2+}]}$$

where the total CEC at the relevant pH is: $CEC = CEC1 + CEC2 + CEC3$

Such an approximation is presented by the dotted lines in Fig. 3.6. It is seen that most of the experimental features can be represented reasonably well by the combination of three normal Langmuir isolines. These may, for example, represent separate types of sites on the same clay mineral but could of course also reflect the presence of small amounts of special minerals with particular affinities to Cd.

The selected values for the CEC's and $K_{Cd/Ca}$'s are given on the figure. Most of the total CEC is accounted for by the CEC1 value, but the contribution from this part of the total capacity is practically nil at the low Cd concentrations covered by the figure.

That the Freundlich isolines can be represented as a sum of Langmuir isolines is not a new observation. For example, a theoretical derivation is given in /31/ referring back to an article in Zeitscrift für physikaliche Chemie from 1938 /32/.

3.4.3.3. The Zn/Ca system.

Results for a similar experiment with Zn adsorption and desorption in the same three types of $CaCl_2$ solutions are presented in Fig. 3.7. For Zn the deviation from simple adsorption is even more pronounced than for Cd, but since the Zn concentration in the soil is 59 ppm the use of a model corresponding to the lines with slope 1 in Fig. 3.7. may not give too incorrect solution concentrations as long as the soil concentrations are changed only moderately. However, as pointed out in Section 3.3. the experimentally determined $K_{Zn/Ca}$ value is likely to give too high calculated Zn concentrations in the soil water compared with what was actually found in the soil water samples.

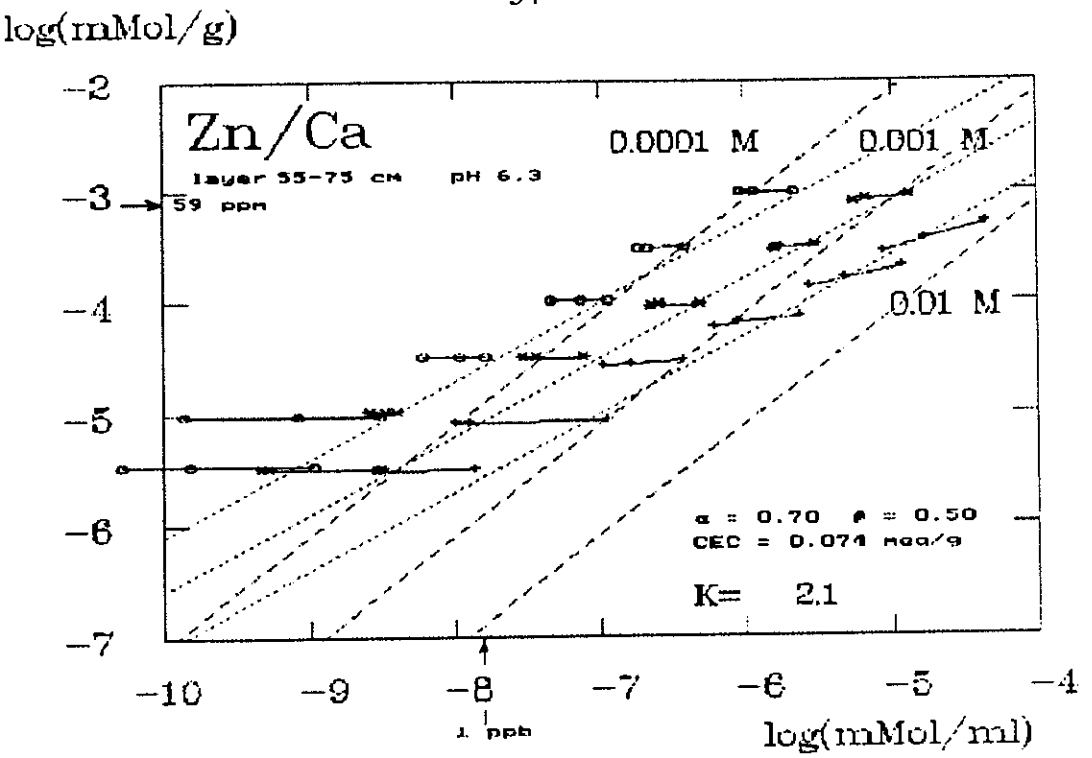

Fig. 3.6. Results from adsorption and desorption experiments using ^{65}Zn in soil from layer 55-75 cm and addition of different amounts of Zn at three different Ca^{2+} concentrations. Each group of three points represents one adsorption (to the right) and two desorption equilibrations. The dashed lines represents Langmuir approximations while the dotted lines are from a Freundlich expression using parameter values indicated in the figures bottom right corner.

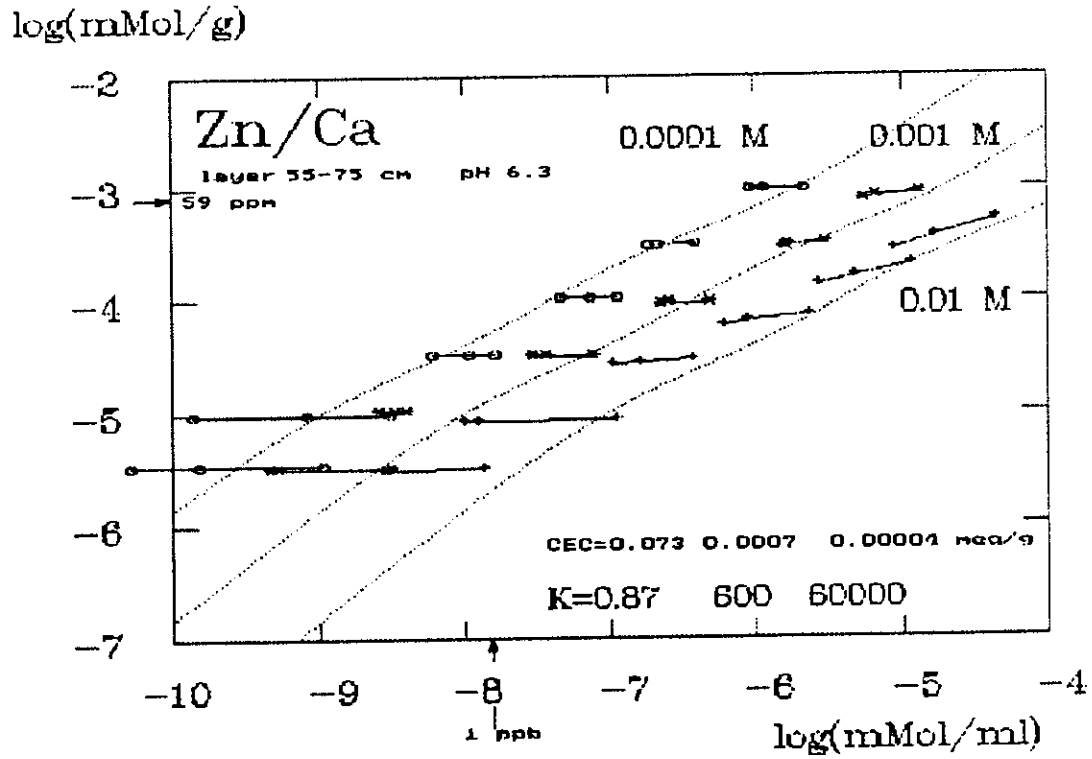

Fig. 3.7. Same results as above but approximated with a "multi-Langmuir" expression using the three set of CEC and K parameters indicated on the figure. The 59 ppm indicated on the ordinate is the actual total concentration of Zn found in this soil.

A good approximation to the whole series of results is obtained with a Freundlich type expression:

$$\log[CdX_2] = \log(0.5 \cdot 0.075 \cdot 2.11) - 0.5 \cdot \log[Ca^{2+}] + 0.7 \cdot \log[Cd^{2+}]$$

A simulation based on the sum of three Langmuir isolines is also possible as illustrated by Fig. 3.7. About 1 % of the total capacity is assumed to have high affinity for Zn: $K2_{Zn/Ca} = 600$ and about 0.05 % extremely high affinity: $K3_{Zn/Ca} = 60000$. These sites will dominate the Zn adsorption at low concentrations. At the higher Zn concentrations the main CEC capacity (~0.073 meq/g) also contributes to the total Zn adsorbed on the soil although the $K1_{Zn/Ca}$ is only ~0.87.

A characteristic of the Zn experiments is that the slope of the lines connecting the adsorption and the two desorption values obtained for each individual system is much lower than the slope of the line connecting the adsorption values. A similar but less pronounced tendency can be seen for Cd in Figs. 3.5. and 3.6.

This difference in behaviour would not be possible if true equilibrium was reached in absorption as well as desorption of the micro-element. The desorption difficulties are probably the explanation of the low Zn-concentrations actually found in soil water samples from the test area, typically about 10-20 ppb or $\sim 2 \cdot 10^{-7}$ mMol/ml, see Section 3.3.

The equilibrium constant K is also defined as the ratio between the rate constants for the forward- and the reverse reactions:

$$Zn^{2+} + CaX_2 \underset{k_R \text{ desorption}}{\overset{\text{absorption } k_F}{\rightleftharpoons}} ZnX_2 + Ca^{2+}$$

$$K = k_F/k_R$$

It follows that a high value of K must be due to a low rate of the reverse reaction relative to the forward reaction. An extreme case would of course be that some of the Zn was fixed irreversibly in a way not available for exchange.

The assumption that the main CEC1 capacity with $K_{Zn/Ca} = \sim 0.9$ and therefore $k_F = \sim k_R$ dominates at higher Zn concentrations while the much smaller CEC1 and CEC2 capacities with high values for the equilibrium constants and therefore $k_F >> k_R$ is dominating at low Zn concentrations may therefore also explain that the deviation from equilibrium behaviour is much more pronounced at low Zn concentrations.

3.4.3.4. Effects of equilibration time.

An experiment has been conducted to see if the adsorption and desorption behaviour would be improved by longer equilibration times. The investigation was restricted to the area around 59 ppm Zn in the solids and the equilibrations were made with 0.001 M $CaCl_2$ only. The results are shown in Fig. 3.8. The dashed line is the same as the line with slope 1 for 0.001 M Ca^{2+} in Fig. 3.7. and the two set of results marked as • are also from this figure.

The two set of points marked by: ₀ and o, respectively, show that the increase of adsorption equilibration from 2 hours (with shaking) to 14 days (with shaking 1 h each day) decreases the Zn concentration in the solution about a factor 2.

The results for the systems equilibrated according to the selected standard procedure (1 h shaking + standing to next day + 1 h shaking, points marked x, X or •) or equilibrated for 7 days (with shaking 1 h each day, marked + or #) gave - at least at the higher Zn concentration - more or less the same results as for the ones marked ₀ and o.

The effect of varying the desorption time from the 1 day standard procedure to 7 days is not clear. Probably the increase in time is too small to give significant differences.

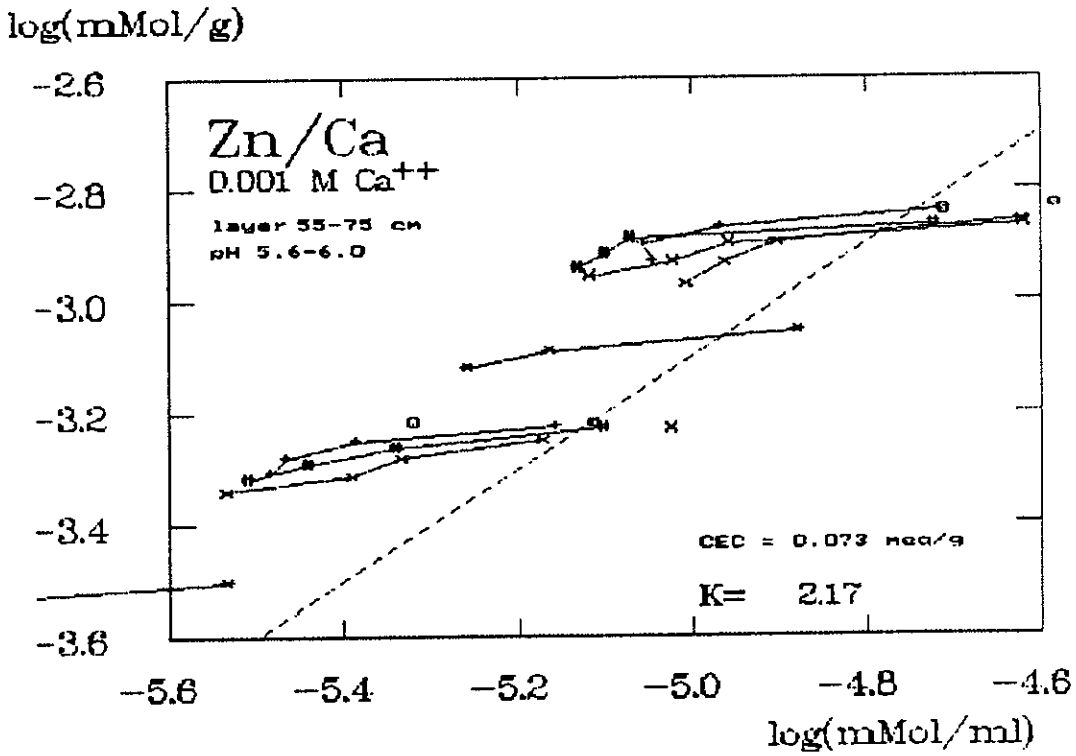

Fig. 3.8. Results from adsorption and desorption experiments using different equilibration times: from 2 hours to a fortnight, see text for details. ^{65}Zn was added to soil from layer 55-75 cm together with different amounts of Zn in 0.001 M Ca^{2+} solution. Each group of three or four points represents one adsorption (to the right) and two or three desorption equilibrations. The dashed lines is the Langmuir approximation for 0.001 M Ca^{2+} shown in Fig. 3.6.

At low concentrations ion exchange sites with high K values may well require months or even years to reach desorption equilibrium. At the higher concentrations investigated here, it appears characteristic that the first desorption step results in a relatively large decrease in solution concentration while the following values lay on lines with higher slope even approaching 1 for the systems with highest Zn contents.

The investigation is insufficient to elucidate the desorption behaviour. Some improvements in calculating actual soil concentrations may be obtained by using desorption instead of adsorption measurements to obtain the K values. However, the calculated concentrations are still likely to be too high.

3.4.3.5. Variation with depth.

As described previously, soil samples taken from 5 layers on top of each other are available from the test area (see Table 3.9., etc.). The results of Zn/Ca equilibration measuremens for samples from these 5 layers in 0.001 M Ca^{2+} are shown in Fig. 3.9. For clarity only the absorption measurements are included. It is seen that the soils behaves rather similarly at high Zn concentrations while the slope of the curves is decreasing systematically with increasing depth of the soil layer. This may indicate that the high affinity sites for Zn are in some way associated with the clay mineral fraction (content increasing with depth) and not with the organic fraction or Mn content (decreasing with depth).

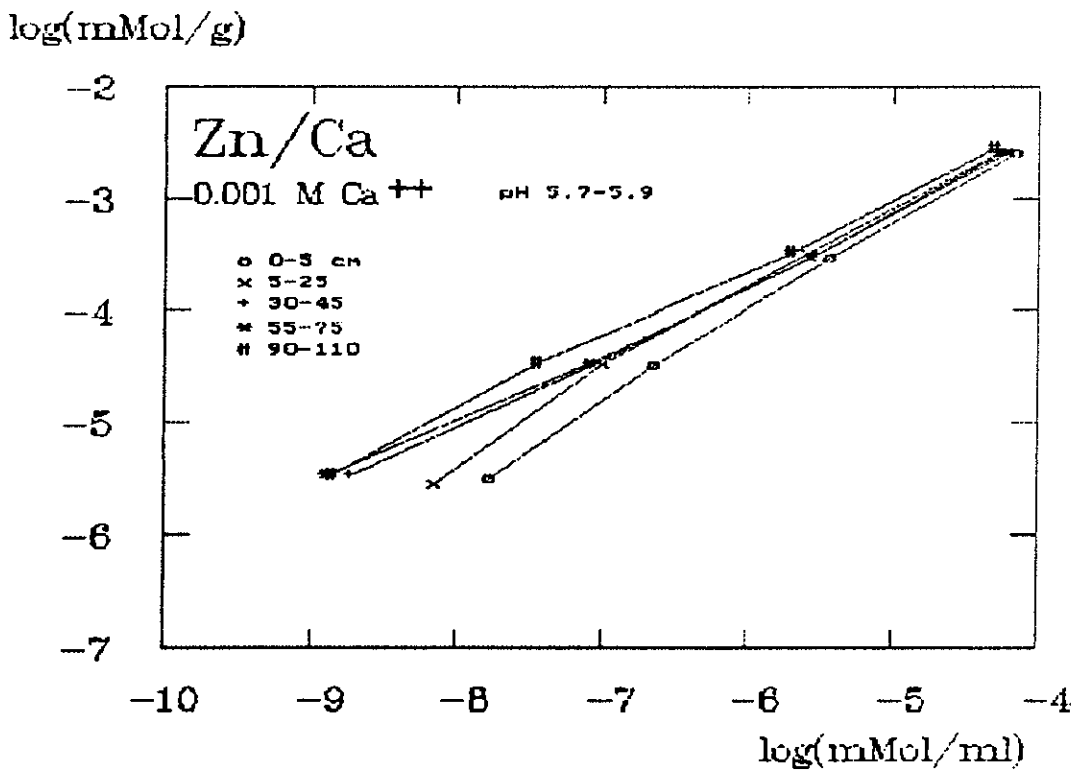

Fig. 3.9. Results from adsorption experiments with ^{65}Zn and different amounts of Zn in 0.001 M Ca^{2+} solution added to soil samples from the 5 soil layers from the selected pit.

3.4.3.6. Variation with pH.

Finally the effect of pH changes on the Zn/Ca equilibrium for soil samples from layer at 55-75 cm were investigated in 0.001 M Ca^{2+}. The soil samples were pre-equilibrated with HCl-containing $CaCl_2$ solutions to give pH 5.7, 5.2, 4.5 and 3.4, respectively. The pH could be maintained constant within ± 0.1 to 0.2 units during the absorption and the following two desorption steps.

The results are shown in Fig 3.10. It is seen that the affinity of the soil for Zn decreases systematically with pH and that the effect is most pronounced at the lower Zn concentration maybe indicating that the small amounts of high affinity sites are destroyed by the acid. A study of the reversibility of the effect would be interesting. At pH 3.4 the slope of the curve is nearly one (as indicated by the dashed line in the figure) and even the desorption behaviour is well described by this line. A more exact fit can be obtained using Freundlich isolines, and the parameter variation with pH can easily be derived from the figure.

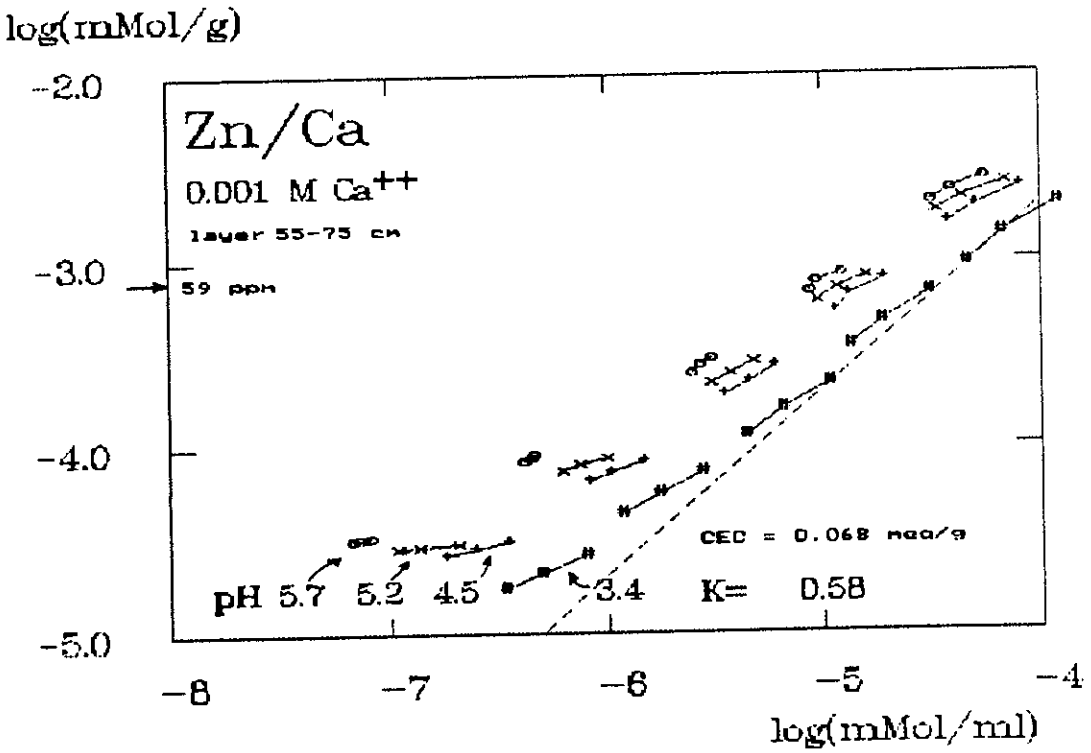

Fig. 3.10. Results from adsorption and desorption experiments with soil from layer 55-75 cm preequilibrated to different pH. ^{65}Zn was added to the soil together with different amounts of Zn in 0.001 M Ca^{2+} solution. Each group of three points represents one adsorption (to the right) and two desorption equilibrations. The dashed line is a Langmuir approximation for the most acid systems (pH ~3.4) using the CEC and K values indicated on the figure.

3.4.4. Mg/Ca, K/Ca, Na/Ca ion exchange equilibria.

As a supplement to the experiments with Cd and Zn ion exchange some tentative determinations of equilibrium constants for Mg/Ca, K/Ca and Na/Ca have also been made for soil samples from the layer at 55-75 cm. The procedure was similar to the one mentioned in Section 3.4.3. but only the adsorption step was made and non-active Mg, K or Na solutions were employed for the equilibration after Ca saturation in 10^{-2}, 10^{-3} or 10^{-4} M $CaCl_2$, respectively. Control analyses of the last pure $CaCl_2$ solution from the saturation procedure show slight continuing releases of Mg, K and Na, probably due to degradation of various minerals in the soil. This makes the determination of the amounts of adsorbed Mg, K or Na rather uncertain especially at low concentrations, since they are calculated as the difference between the contents in solution before and after equilibration.

The usable experimental results are plotted in Figs. 3.11 and 12. for Mg and K, respectively. K-values corresponding to the reaction:

$$Mg^{2+} + CaX_2 = Ca^{2+} + MgX_2$$

and the expressions:

$$\frac{[MgX_2]\,[Ca^{2+}]}{[Mg^{2+}]\,[CaX_2]} = K_{Mg/Ca}$$

$$2\cdot(CaX_2 + MgX_2) = CEC$$

or for monovalent ions:

$$2\,Na^{+} + CaX_2 = Ca^{2+} + 2\,NaX$$

$$\frac{[KX]^2\,[Ca^{2+}]}{[K^{+}]^2\,[CaX_2]} = K_{K/Ca}$$

$$2\cdot CaX_2 + KX = CEC$$

are given on the figures calculated for a CEC value of 7.3 meq/100 g of soil from this layer at pH ~6, see Fig 3.4. The dashed lines are the simplified linear approximations to the expressions assuming e.g. $[Ca^{2+}]/K_{Mg/Ca} >> [Mg^{2+}]$.

The value for $K_{Mg/Ca} = 0.42$ or $K_{Ca/Mg} = 2.4$ for the reversed reaction is in reasonable agreement with the value 3 proposed for this reaction in /29/. For potassium $K_{K/Ca} = 6.7$ indicates some preference of adsorption of this element compared with calcium. For sodium the opposite is the case but the experimental results are very uncertain: $K_{Na/Ca} = 0.01$ may be assumed. These values were used in the simulations in Section 4.

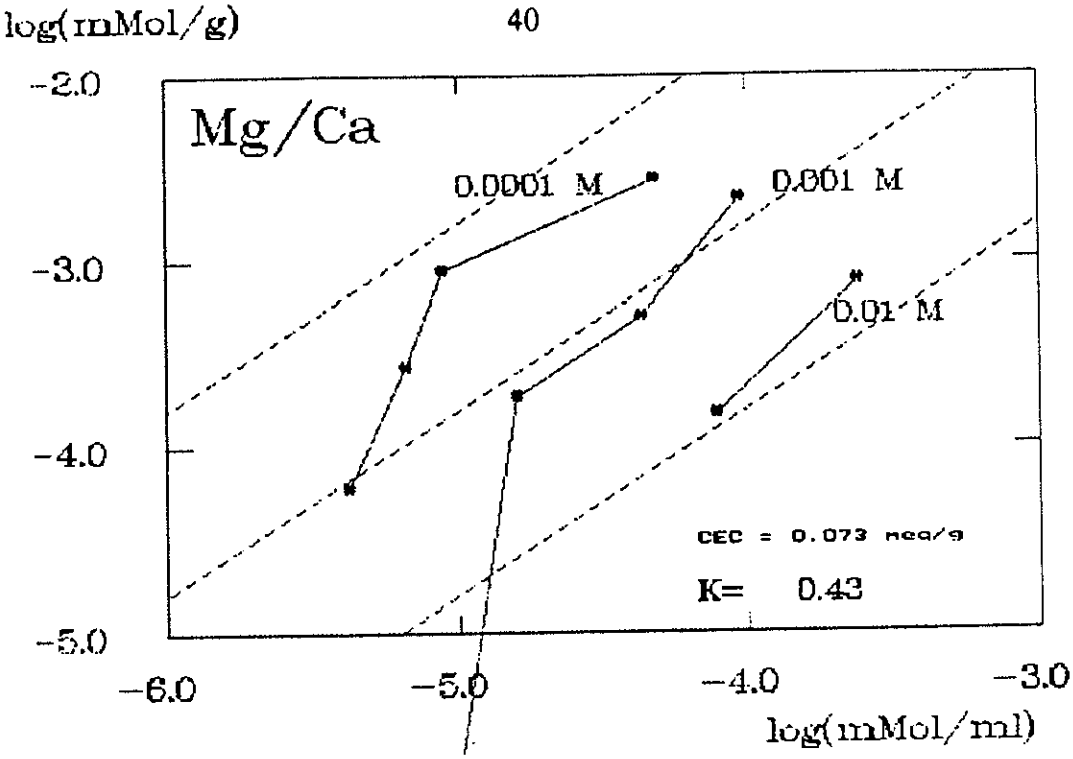

Fig. 3.11. Results from magnesium adsorption experiments at pH ~6 with soil from layer 55-75 cm. Mg^{2+} was added in different amounts to soil pre-equilibrated with Ca^{2+} at three different concentrations. The dashed lines represent Langmuir approximations using the parameter values given in the figure.

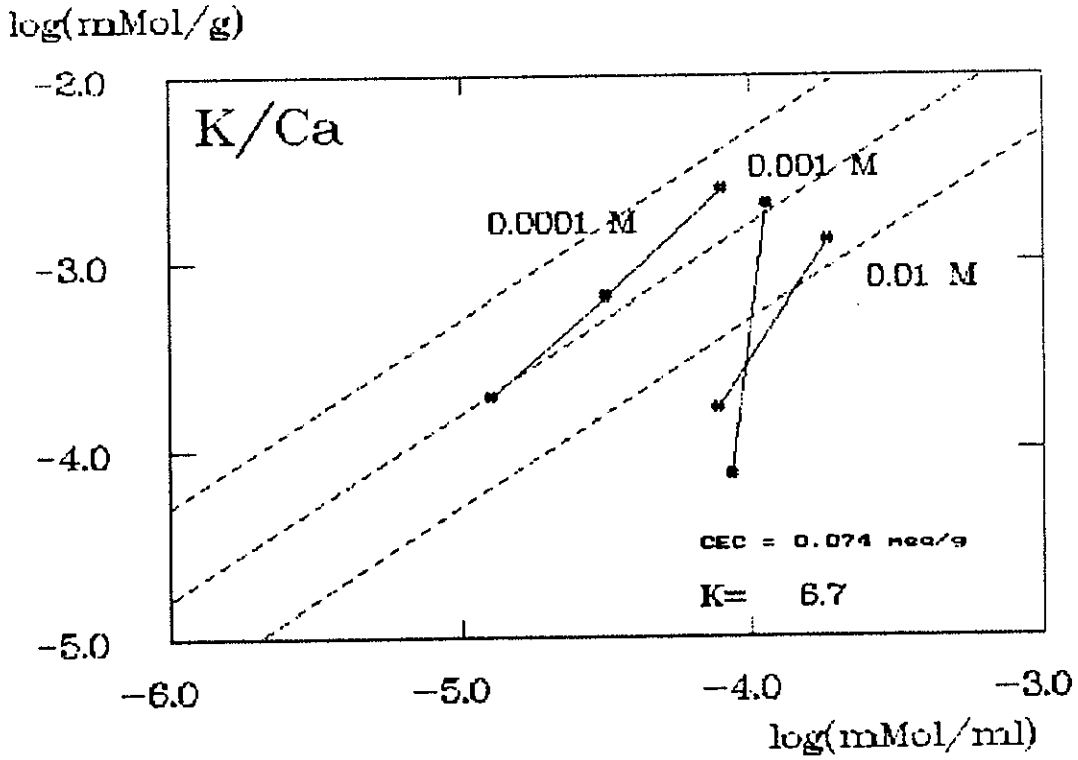

Fig. 3.12. Results from potassium adsorption experiments at pH ~6 with soil from layer 55-75 cm. K^{+} was added in different amounts to soil pre-equilibrated with Ca^{2+} at three different concentrations. The dashed lines represent Langmuir approximations using the parameter values given in the figure.

3.4.5. Total contents of acid-extractable cations.

Concentration profiles for the different materials bound to or in the soil particles give a picture of the present status of the soil layers. The profiles are determined by the composition of the original rock sources and geological sorting and settling mechanisms together with later processes such as plant growth, leaching, weathering, precipitation and maybe pollution.

Experimentally the concentration profiles at the selected site in the Frederikborg test area have been determined by boiling material from the 5 sampled soil layers for 8 hours in half-concentrated super-pure nitric acid followed by (partial) digestion of undissolved material in HF + H_2SO_4. The extracts were analysed by AAS or ICP-MS.

Boiling in strong HNO_3 is often regarded as sufficient to obtain an impression of the content of micro-components in a soil sample. This has been investigated systematically for a large number of Danish soils /33/. Hydrofluoric acid digestion should in principle result in complete dissolution, but this was not quite attained here.

Table 3.11. gives the combined contents of materials dissolved by both treatments. The fraction of the total amounts found in the nitric acid extracts are also given as mean values over all 5 layers. It is seen that Na, K and to some degree Ca are only incompletely extracted by HNO_3 alone. This is probably because a considerable part of these elements are present as feldspar minerals. Mg, Fe, Mn and most of the minor components are mainly found in the nitric acid extract and may to some degree be associated with the same acid-degradable minerals. Cd shows (as the only element) a systematic decrease from 76 % to 33 % extractable by HNO_3 when going from the top to the bottom layer. However, the analytical uncertainty is considerable for this element and control experiments to test the unexpected low degree of acid extraction ought to be made.

The contents given for layer 5-25 cm are used as the basis for the acid extraction leach curves discussed in Section 3.5.

Table 3.11. Total contents of cations in soil samples from the 5 layers in the selected pit at the test area in Frederiksborg forest district. (The low Cd recovery in the HNO_3 extract makes the results for this element somewhat dubious.)

Soil sample from layer:	Sum of HNO_3 and $HF+H_2SO_4$ extract analyses recalculated as ppm in dry soil											
	AAS					ICP-MS						
	Na	K	Ca	Mg	Fe	V	Mn	Cu	Zn	Cd	Pb	U
0 - 5 cm	7750	12800	4190	3030	14700	32	740	10	55	0.25	16.3	1.3
5 - 25 cm	11500	22600	5330	3600	19700	48	670	19	56	0.21	8.8	1.7
30 - 45 cm	10700	24300	6460	5400	26900	73	500	25	63	0.20	9.9	1.9
55 - 75 cm	10800	23900	6190	5300	27900	69	420	23	59	0.17	6.8	1.6
90 - 110 cm	14500	26000	5520	6100	31200	74	460	24	60	0.21	6.9	1.7
% of total found in HNO_3 extract:	8	19	~43	83	86	75	84	61	80	53	~100	41

A graphical presentation of the HNO_3 extractable contents in the soil layers is given in Fig.3.13. It is characteristic for most of the elements that the acid extractable contents are lowest in the top soil layers reflecting that rain water leaching is faster than the rate of upward movement due to plant turn over. However, the opposite appears to be the case for Mn. As far as Pb and perhaps Cd are concerned, the increased levels in the top layer are probably due to the accumulative effects of long-term air pollution.

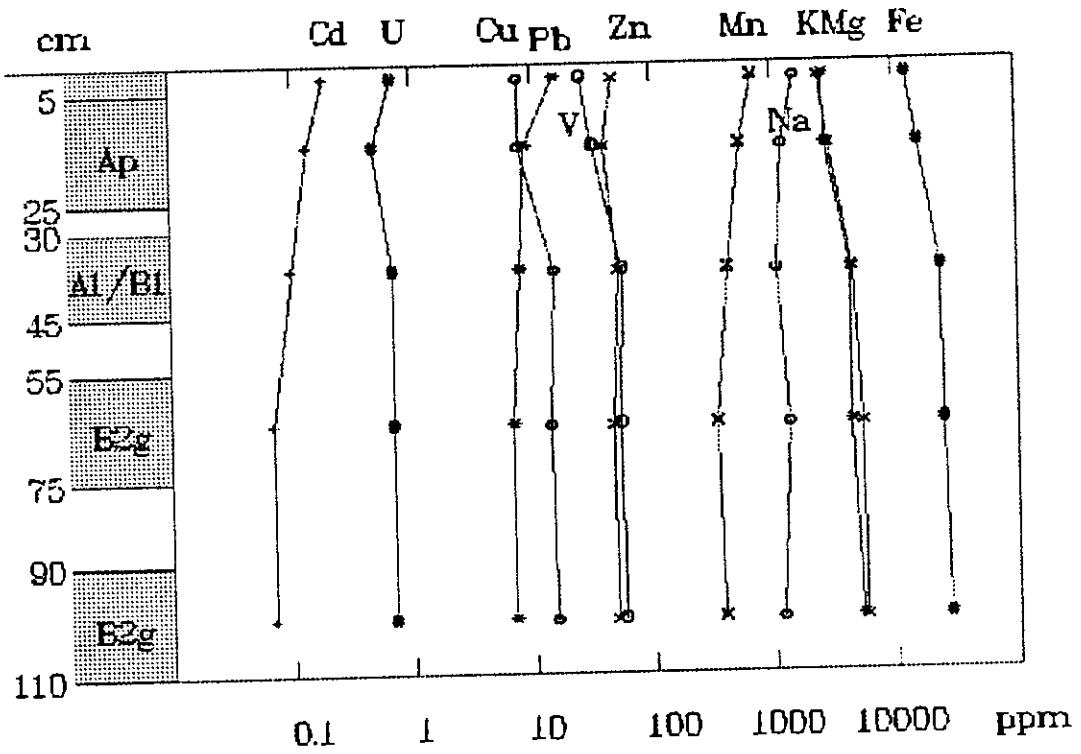

Fig. 3.13. The analyses from Table 3.11. plotted as profiles against the depths where the soil samples were taken.

3.5. Extraction series.

An experiment with accelerated acidification of soil from the area has also been made as a supplement to the field data.

The methodology was developed previously. Four samples of soil (Systems I and II: 35 g and III and IV: 70 g) from the 5-25 cm layer were placed in 160 ml polypropylene centrifuge flasks and 140 ml water was added corresponding to a water/soil ratio of 4 or 2. The soil particles were kept in suspension by rotating the flasks in an inclined position while moist compressed air was bubbled trough the suspension.

In closed flask as well as in situ soil, bacterial degradation of organic material in the soil may give rise to quite high, but rather undefined values for the CO_2 pressure. In the open systems employed here the air bubbling ensures a fixed value for this parameter, and this is important, at least at high pH values. Ordinary compressed air was used i.e. $pCO_2 = 0.0003$ atm., but the equipment has previously been used to study systems in equilibrium with air at higher CO_2 pressures.

The 4 systems were equilibrated for 24 hours followed by
- centrifugation (with closed caps),
- sampling of 50 ml clear solution - which was replaced by 50 ml ultrapure (systems I and III) 0.0018 M or (II and IV) 0.0036 M H_2SO_4, - resuspension of the soil and
- equilibration for a new 24 hours period.

The procedure was repeated 16 times, the 3 last times with the equilibration periods extended to between 10 and 14 days.

The solution samples were analysed for pH and for Ca, Mg, Na, K by AAS and for Al, Mn, Cu, Zn, As, Cd, Pb by ICP-MS. The values for As were in general below the detection limit. Also the values for Cd and Cu are rather uncertain.

System I can, for example, be regarded as corresponding to a soil layer of 70 kg/m^2 or about 28 mm soil with (suspended in) 140 mm 'pore' water and exposed to 50 mm 'acid rain' per timestep or in total 800 mm for the 16 additions of acid in the experiment. In total the acid exposure was 4.1 meq H^+/100 g soil i.e. of the same order as the CECP value found for this soil layer, see Table 3.10. The acid exposure corresponds to ~40000 meq H^+/m^2 for a 250 mm thick soil layer (1.5 g/cm^3) or about 200-400 years exposure to 'normal' acid rain.

The soils in systems II and III are both exposed to twice as much acid, the only difference being that the soil/solution ratio is a factor 2 higher for system II and the acid concentration a factor 2 lower.

For the soil in system IV the amount of acid is again doubled corresponding to 16.5 meq H^+/100 g soil i.e. considerably more than the CECP+CECV value.

The results are given in graphical form in Figs. 3.14b,c,d and 3.15a,b,c,d as accumulative leached fractions ($\Sigma a/ao$ %) of the total HNO_3+HF extractable amounts (ao) previously found to be present in the soil, see Table 3.11. Values for total Al were not determined and a content of 10% Al has been arbitrarily assumed.

It is seen that only about 10% of the total Ca is extractable under these experimental conditions. The level is the same for all 4 systems and is reached after exposure to practically the same amounts of acid. It may be concluded that it is mainly the Ca bound to ion exchange sites which is released by the treatment. The dissolution of the remaining ~90% Ca occurs very slowly at a rate corresponding to about 0.05 to 0.2 % Ca per ml/g solution contacting the soil.

The other macro-cations: K, Na and Mg do not show such a pronounced initial ion exchange behaviour. They are released at a more uniform rate resulting in nearly straight-line leach curves as seen in Figs. 3.14a,b,c,d. It should be noticed that the

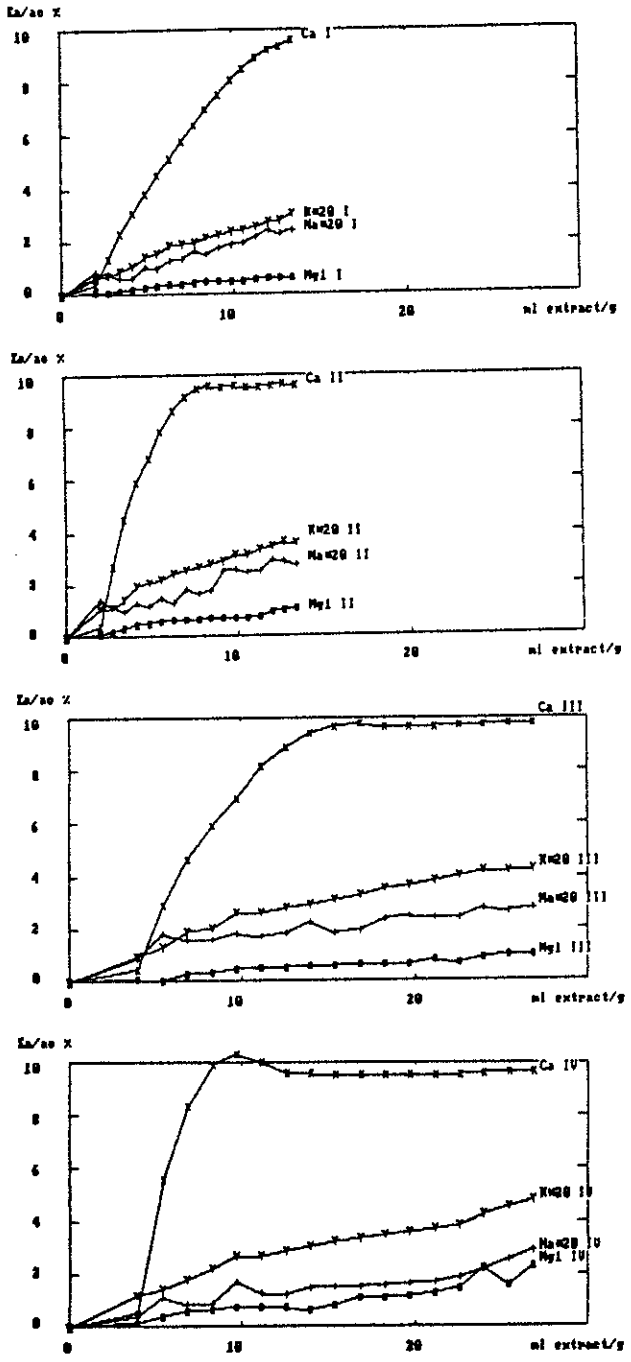

Fig. 3.14a,b,c,d.
Leach curves for acid extraction of macro-components from soil samples from layer 5-25 cm

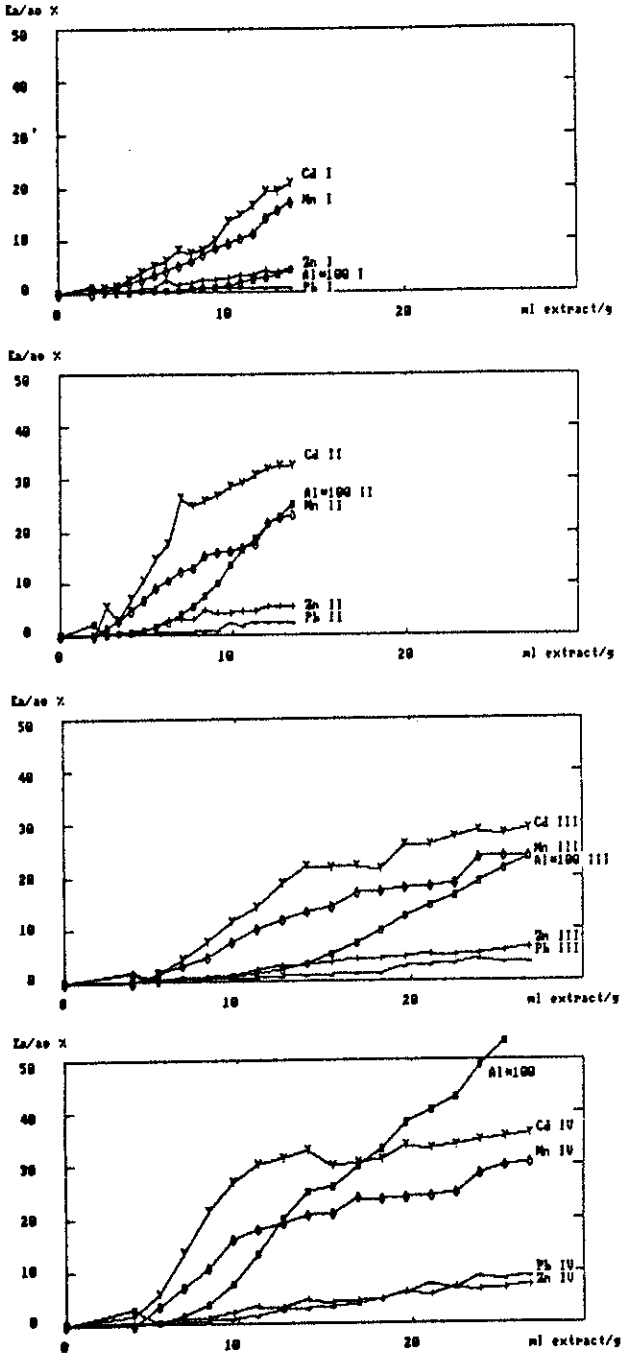

Fig. 3.15a,b,c,d.
Leach curves for acid extraction of micro-components from soil samples from layer 5-25 cm.

System I

70 g soil
extracted by
140 ml water
+ 16 · 50 ml
0.0018 M H_2SO_4

System II

70 g soil
extracted by
140 ml water
+ 16 · 50 ml
0.0036 M H_2SO_4

System III

35 g soil
extracted by
140 ml water
+ 16 · 50 ml
0.0018 M H_2SO_4

System IV

35 g soil
extracted by
140 ml water
+ 16 · 50 ml
0.0036 M H_2SO_4

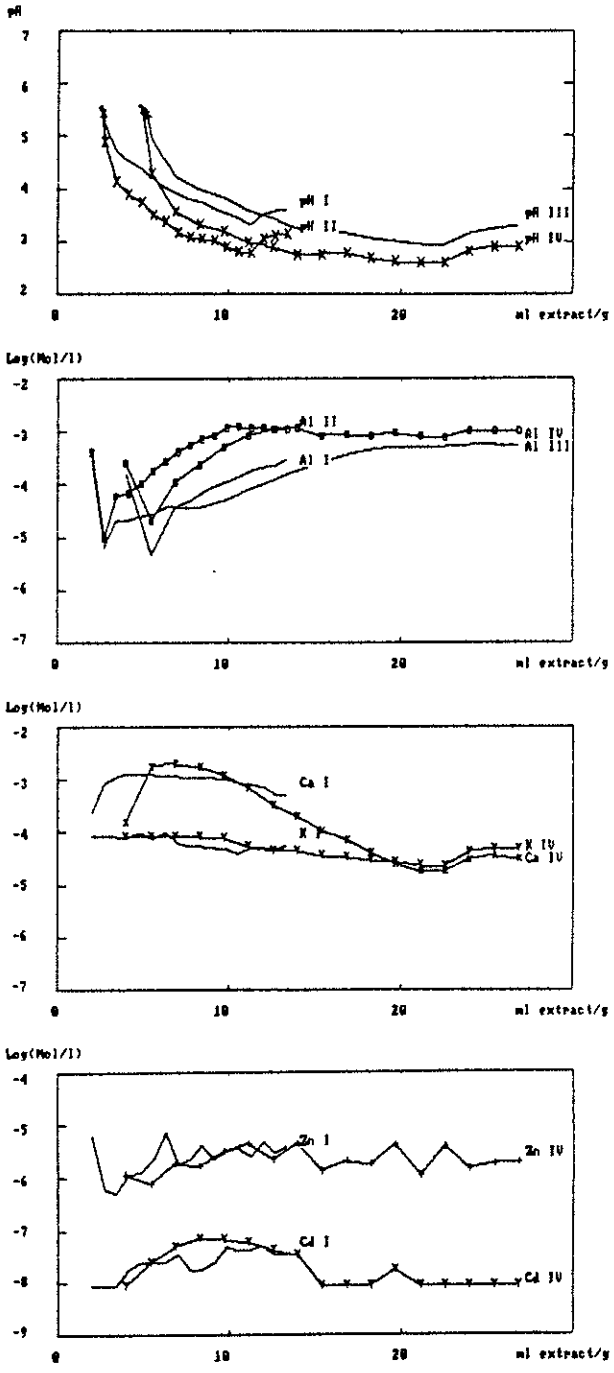

Fig. 3.16a,b,c,d.
Development of pH and Al-concentrations for all four systems and of selected concentrations for systems I and IV.

equilibration time before the 3 last points on the curves are ~14 days or more than 10 times longer than between the previous points. However, the slope of the curves are more or less uniform for systems No. I, II and III over the last ~15 points. This indicates that a contact time of ~1 day is sufficient to reach reasonably constant concentrations, for example determined by equilibrium with the minerals in the soil, so that the released amounts of materials are proportional to the volume of solution which has contacted the soil.

Only for the most acid system, No. IV, is a significant time dependence a possibility for the extraction rate: The slope of the leach curve is about a factor 2 higher for the last 3 points compared with the previous part of the curve. There may, however be other explanations for the phenomenon.

Fig.3.16c shows the measured Ca and K concentrations for the least and the most acid systems: Nos. I and IV,respectively. It is seen that the Ca concentration remains high and reasonably constant around 10^{-3} M as long as the ion exchange capacity is not exhausted. It is thereafter declining (with a slope corresponding to the dilution factor 50 ml out of 140 ml) to values nearly two decades lower. The potasium concentration is much less influenced by the exhaustion of the ion exchange capacity: the concentration declines by only a factor 2 to 3, indicating that a major part of the K ions are supplied by weathering of minerals in the soil.

Longer equilibration time results in about a factor 2 higher K- and Ca-concentrations in the most acid system (3 last points on curves IV), but has only minor effect on the concentrations in the other systems.

Fig. 3.16a shows the pH development for all 4 systems and Fig. 3.16b the corresponding Al concentrations. (The high initial values for Al in all 4 systems are due to suspended colloidal materials: 140 ml pure water was used to start the extraction series and the centrifugation procedure was not sufficent to obtain completely clear samples of the resulting weak ionic-strength solutions.)

All the systems show some pH recovery (0.3 to 0.4 units) during the final long term equilibration periods but this is practically not reflected in the Al-concentrations. Otherwise it is seen that the Al-concentration increases more or less proportionally with the hydrogen-ion concentration as given by pH. The regulating mechanism can therefore not only be dissolution of gibbsite: $Al(OH)_3$ according to

$$Al(OH)_3 + 3\,H^+ = Al^{3+} + 3\,H_2O$$

which would give Al-concentrations proportional to $[H^+]^3$ and - for the normally assumed solubility value of $10^{-33.5}$ - much too high Al concentrations at low pH value compared with the experimental results.

A simple way to simulate the experimental values is to postulate a solubility value for gibbsite of 10^{-36} so that

$$\log(Al^{3+}) = 6 - 3 \cdot pH$$

Futhermore it could be assumed that the speciation in the pH range 3.5 - 7 is dominated by $Al(OH)_2^+$ given by

$$\log(Al(OH)_2^+) = - 0.4 - pH$$

which in this range would result in the observed proportionality between the hydrogen and the total Al concentrations. Such modifications would be easy to include in the ECCES system. However, due to low total Al concentrations it is not very important for the system behaviour at high pH, and the modification was therefore not made before the calculations presented in Section 4.

Some weathering of e.g. potassium feldspar (microcline) to kaolinite:

$$2\ KAlSi_3O_8 + 2\ H^+ + H_2O = Al_2Si_2O_5(OH)_4 + 2\ K^+ + 4\ SiO_2$$

must also be assumed and similar reactions may be postulated for plagioclase, the mixed Na,Ca feldspars, explaining the releases of K^+, Na^+ and also Ca^{2+} after exhaustion of the ion exchange capacity.

Dissolution of a Mg-containing mineral must also be assumed to explain the shape of the Mg leach curves. Dissolution of chlorite: $(Mg,Fe,Al)_6(Al,Si)_4O_{10}(OH)_8$ or conversion of Mg-containing montmorillonite to kaolinite are possibilities.

Figs. 3.15a,b,c,d show the leach curves for Al and for some of the minor components in the soil. The degree of Al leaching reflects the pH status of the four systems but even in the highly acid system IV only about 0.5 % of the estimated total Al-content is solubilized.

Mn (and probably also Fe, which was not investigated) is seen to be much more susceptible to acid extraction since from 15 to 30 % of the total were found in the solutions. Some correlation with the CEC development may be indicated by the shape of the curves but dissolution of, for example, MnO_2 or other Mn-containing minerals must also take place.

Zn and Pb are not very easily extracted even under these extreme circumstances: less than 10 % for system No IV. Again the almost linear leach curves indicate that dissolution of minerals is involved. However, the Zn and Pb may well be present only as minor components in these minerals. Dissolution of small amounts of ion exchange materials with high affinity for e.g. Zn is also a possibility, see Section 3.4.3

A different behaviour is indicated for Cd where a considerable fraction (~20 %) of the total Cd content appears to be released together with Ca during exhaustion of the ion exchange capacity. This is then followed by a linear release rate similar to the values for Zn and Pb.

In Figs. 3.17a and b selected values from the experiments are compared with calculations using the ECCES soil model with appropriate values for hydrology and composition of the 'rain'. The manner of water replacement and the completely mixed systems used in the experiments is in good agreement with the simple hydrology model used in ECCES - much better than for the in situ situation - but other features may not be adequately

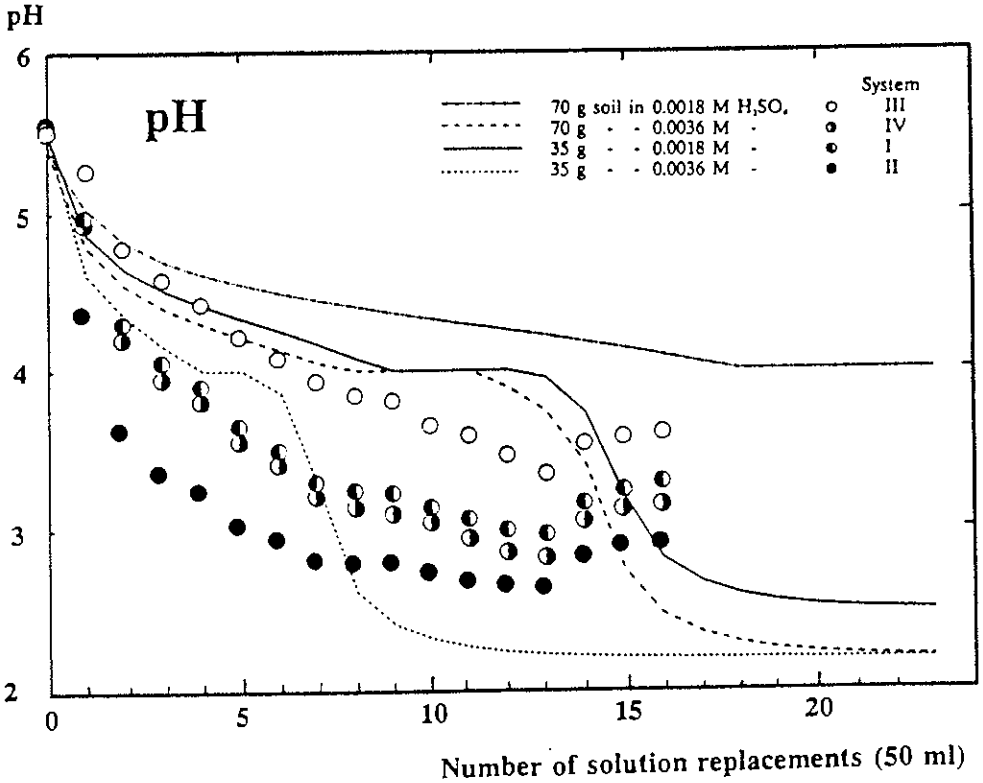

Fig. 3.17a. Comparison of measured pH values from the 4 extraction experiments with the calculated pH development using a modified version of the ECCES soil chemistry code.

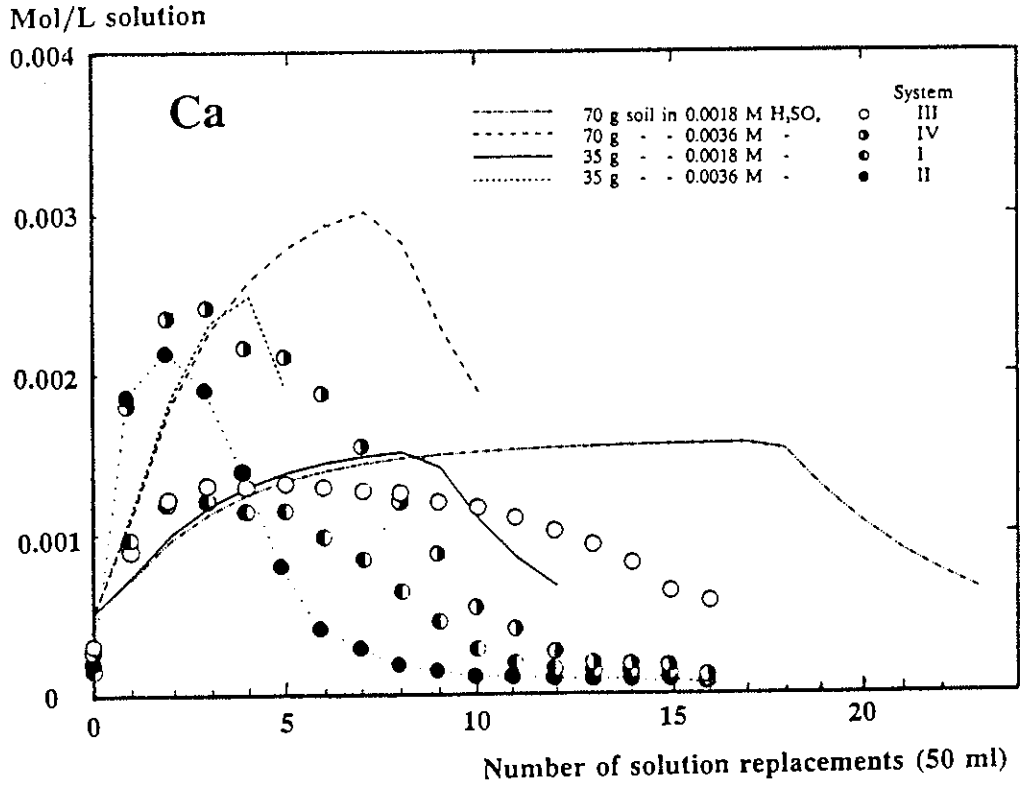

Fig. 3.17b Comparison of the measured Ca-concentrations in solutions from the extraction experiments with calculated values (omitting the later part of the curves).

represented. One possibility is incomplete equilibration due to the relatively short periods of equilibration and the unrealistic high water/solid ratios. Another certain source of error is the omission of weathering reactions for silicate minerals in the ECCES model. Due to lack of time the modification of the Al dissolution behaviour suggested above was not made, resulting in another source of error at low pH values.

In the beginning the measured pH values are about 0.5 pH units lower than the calculated values. Later, when the exchange capacities are exhausted, the calculated values are ~0.3 units lower than the measured. The last phenomenon and the increase in the measured pH for the 3 last points (longer equilibration times) are thought to be due to the above-mentioned incomplete representation of weathering reactions in the model.

In general the trends in the calculated and measured calcium concentrations shown in Fig. 3.17b. are in agreement within a factor 2, but the employed version of the model gave unreasonable Ca-concentrations below pH 4. This may also be reflected in the pronounced "shoulder" on the pH curves at this value in Fig. 3.17a. Manpower limitations have prevented the identification of the error(s), but the calculations will be rerun when a new PC-version of the soil chemistry model is operational.

4. MODELLING

4.1. The ECCES forest model.

As part of the EFP-85 project, see /1/ the ECCES-model was extended with a forest module. This new module simulates in rather simple terms the changes which occur in the composition of rainwater when it comes into contact with the forest canopy and with decaying litter on the forest floor. The most important phenomena taken into account in the forest module are:

1) Dry deposition in forest areas is about 2 to 3 times as large as on open land because of the larger surface roughness.

2) Interception in the canopy reduces the amount of water reaching the soil.

3) Decomposition of organic matter on the forest floor increases the input of pollutants to the soil.

In the implementation of the above-mentioned processes some basic assumptions have been made. First of all, the forest system is considered to be static, i.e. there is no net growth in the biomass from one year to the next. This implies that all uptake of pollutants from the soil will be returned with the litter-fall.

Secondly, the total evapotranspiration is assumed to be 70 % of the total precipitation. The evapotranspiration for each month is calculated according to an empirical distribution.

It must be stressed that the purpose of the forest module is to calculate the amounts of precipitation and deposition actually reaching the forest soil, rather than to give a detailed description of the processes in the canopy. Thus the main emphasis in the simulations is still on soil chemistry.

A more comprehensive description of the forest model is given in /1/.

4.2. Special application to the test area.

One of the main tasks of this project is the application of the ECCES-model to the test area. Since the monitoring programme (comprising measurements of air pollution, dry and wet deposition, throughfall, litterfall and soil-water composition) was started in 1985, this year was selected as the initial year in the simulations.

Two types of simulations have been run:

1) Short-term simulations (5 years) with one-month time steps to provide the best data for comparison with the experimental data.

2) Long-term simulations (30-100 years) with one-year time steps to examine the long-term development in the test area.

All simulations are performed with the same annual amount of deposition, precipitation etc., as it has not been possible to use data for the separate years in the monitoring period. In the following sections documentation for the input data used in the simulations will be given. Simulations are only carried through for the beech plot.

4.2.1. Soil characteristics.

In the first part of this project a number of soil samples were collected and characterised, see Sections 2 and 3 and ref. /2/. The main parameters from this work used in the simulations are shown in Table 4.1.

As noted in Section 3.4.2. the previously used relationship between pH and CECV /29/ based on the $CECV_{max}$ gives a rather poor representation of CECV around the pH of interest. The modified $CECV_{max}$ has therefore been introduced in the simulations.

Table 4.1. Soil characteristics for Frederiksborg forest district. All data are experimental values reported in /2/ except for density /35/ and CECV (Section 3.4.2. in this report).

Soil layer	(cm)	0-25	25-50	50-75	75-110
Soil content	(mm)	147	154	158	217
Max. water cont.	(mm)	87.5	75	75	112
Min. water cont.	(mm)	22.5	27.5	32.5	52.5
Density	(kg/l)	2.64	2.71	2.71	2.71
CECV (mod.)	(meq/100 g)	2.9	2.5	1.0	1.0
CECP	(meq/100 g)	4.1	6.6	6.8	8.0
Organic carbon	(mg C/g soil)	7.6	2.0	1.2	1.2
React. MnO_x	(mg Mn/g soil)	0.53	0.41	0.34	0.38
Clay content	(%)	14.5	15.6	20.1	24.7
Root distrib.	(%)	44.0	41.3	9.1	5.6
pH		5.4	5.9	6.0	6.0

4.2.2. Soil water composition.

Start concentrations in the soil water used in the simulations are given in Table 4.2. These data were obtained in the start of the monitoring programme from lysimeter samples collected in a depth of 90 cm. The start concentrations for all ions except for H^+ and Cl^- are assumed to be constant throughout the soil layers. In the simulations the start "concentrations" on the ion exchange sites are calculated on the basis of these concentrations. It is therefore particularly important for short-term calculations that the start concentrations are accurate.

4.2.3. Adsorption to the ion exchanger and uptake in plants

The concentrations of ions on the ion exchanger are calculated from the distribution coefficients, which describe the adsorption in relation to calcium (as explained in Section 3.4.4.). However, in the model the coefficients for the reversed reactions are used, which means that reciprocal values are employed and a coefficient less than one corresponds to a preference of adsorption compared to calcium.

Table 4.2. Soil water concentrations for Frederiksborg forest district. The H^+-concentration is calculated from pH measurements on soil samples /2/. The other concentrations are measurements on soil-water samples taken from /9/, except Zn^{2+} which is from /2/.

Soil layer (cm)	0-25	25-50	50-75	75-110
Concentration (mMol/l):				
H^+	0.00398	0.00126	0.001	0.001
Ca^{2+}	0.516	0.516	0.516	0.516
Mg^{2+}	0.124	0.124	0.124	0.124
Na^+	0.458	0.458	0.458	0.458
K^+	0.014	0.014	0.014	0.014
Al^{3+}	0.004	0.004	0.004	0.004
Zn^{2+}	2.3E-4	2.3E-4	2.3E-4	2.3E-4
Cl^-	0.896	0.894	0.894	0.894
SO_4^{2-}	0.436	0.436	0.436	0.436

Ion uptake in plants is calculated on the basis of water uptake, the root distribution between the soil layers and an uptake coefficient which determines the uptake in relation to the ion content of the soil water, see /34/. The coefficients used in the simulations are not experimentally validated, but chosen in such a way that the ion uptake is in fair agreement with the measured content in litterfall for the main part of the ions.

The distribution coefficients and water-uptake coefficients used in the simulations are shown in Table 4.3.

Table 4.3. Parameters for adsorption and uptake in plants. Distribution coefficients are for the reversed reactions compared to those mentioned in Section 3.4.4.

Ion	Distribution coeff.	Water uptake coeff.
Ca^{2+}	-	1
Mg^{2+}	2.4	1
Na^+	100	0.1
K^+	0.15	10
Zn^{2+}	-	0
Al^{3+}	-	0
Cl^-	-	1
NO_3^-	-	2
SO_4^{2-}	-	0.2

4.2.4. Meteorological data.

The monthly precipitation used in the simulations is an average for the years 1985-87 and is taken from /36/. As explained in Section 4.1, evapotranspiration is calculated from the precipitation. In Table 4.4. the calculated values are shown along with the monthly precipitation.

In the model the equilibria constants for a number of chemical reactions are calculated on the basis of temperature. For the present simulations it has been necessary to use estimated values based on literature (shown in Table 4.5.), as the temperature for the different soil layers was not measured in the monitoring programme.

4.2.5. Deposition data.

Deposition data from the monitoring programme is shown in Table 4.6. The indicated proton deposition is the total value comprising both the direct proton deposition and the admission from proton producing compounds, e.g. SO_2.

In the simulations all pollutants are assumed to be dissolved in the rainwater giving the concentrations also shown in Table 4.6.

Table 4.4. Averaged monthly data for precipitation in Frederiksborg, Copenhagen and Roskilde counties for the period 1985-87 /36/ and the corresponding evapotranspiration as assumed in the ECCES-model.

Month	Precipitation (mm)	Evapotranspiration (mm)
January	43	4
February	18	4
March	41	24
April	38	29
May	38	44
June	55	72
July	88	91
August	65	64
September	61	55
October	37	34
November	57	10
December	83	5
Total	624	436

Table 4.5. Soil temperatures /1/.

Soil layer (cm)	0-25	25-50	50-75	75-110
Temperature (°C):				
January	1	3	4	5
February	0	2	3	4
March	1	2	2	3
April	6	4	4	3
May	13	10	8	6
June	19	16	13	10
July	23	19	17	15
August	19	17	18	15
September	16	15	15	15
October	11	12	12	13
November	4	6	9	11
December	4	5	6	7

Table 4.6. Annual deposition for Frederiksborg forest district in the period 1985 to 1987 /9/.

Ion	Total deposition (g/m^2/year)	Concentration (mmol/l)
H^+	0.122	0.194
Ca^{2+}	0.400	0.0160
Mg^{2+}	0.180	0.0119
Na^+	1.40	0.0976
K^+	0.270	0.0111
Zn^{2+}	0.003	7.4E-5
NH_4^+-N	0.790	0.0904
Cl^-	2.48	0.112
SO_4^{2-}-S	1.96	0.0980
NO_3^--N	1.23	0.141

4.3. Example calculations

Before the presentation of results from the model calculations a few points should be noted.

Firstly, litterfall is calculated on the basis of the ion uptake from the soil for the preceeding year. This means that there will be no input of ions from decomposition of litter in the first year of the simulations, and hence that the calculated concentrations are not to be relied upon for the first one or two years of the simulated periods.

Secondly, the way in which the hydrological calculations are performed introduces the artifact that after the first year of a short-term simulation there will be no dry-out of the upper soil layer, as can be seen in Fig. 4.1. In the long-term simulations (with one-year time steps) this effect is even more pronounced, so that all soil layers are continously saturated after the first year.

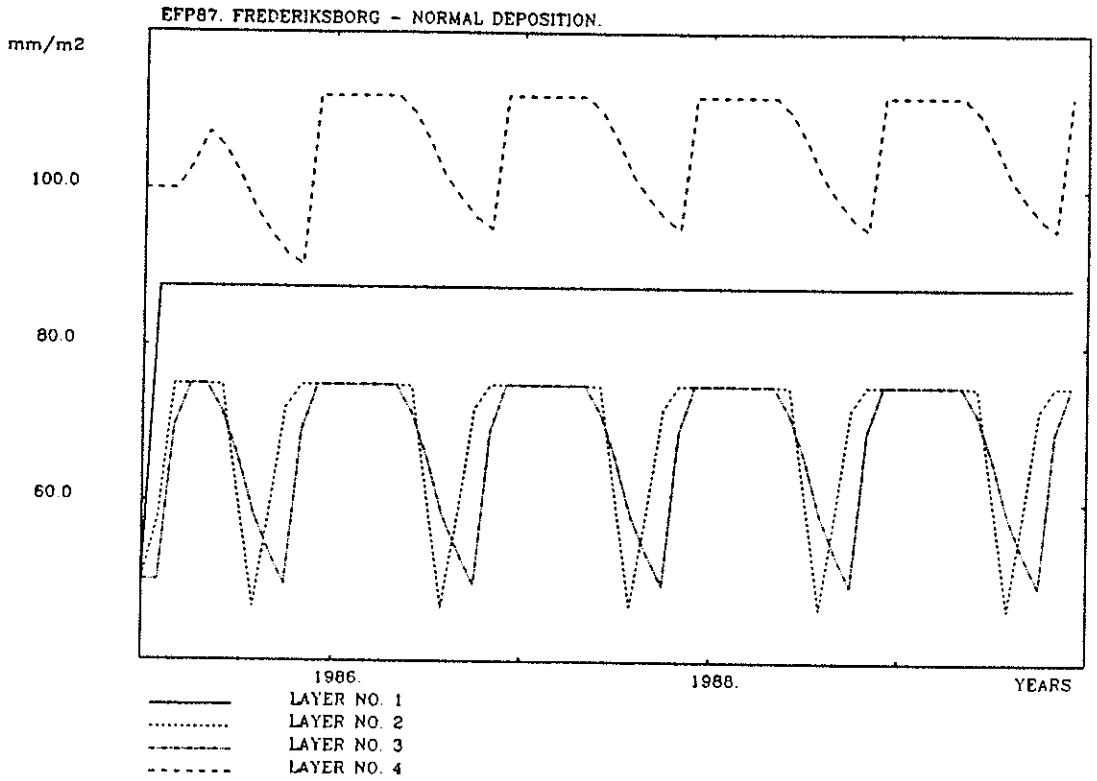

Fig. 4.1. Water content in the soil layers during a short-term simulation.

4.3.1. Comparison of measured and calculated material fluxes.

In Table 4.7. material fluxes out of the root zone are compared. At the experimental site there is balance between the in-flux and out-flux of nitrogen, and the model data shown for this element are therefore taken from the end of the simulation, as in the model all input of nitrogen is converted to nitrate, which is assumed to run through the soil layers without further chemical change.

Table 4.7. Material fluxes out of the root zone. The experimental values are measured in the period June 1985 - June 1986 at a depth of 90 cm /9/. The ECCES results are taken from the fifth year of a 30-year simulation (except for the N-data, which are from the end of the simulation when there is balance between the in-flux and out-flux).

Element	Measured (g/m^2)	Calculated (g/m^2)
Na	2.8	2.1
Mg	1.7	0.59
K	0.14	0.10
Ca	9.1	4.3
N	2.5	2.2
S	3.5	2.2

It can be seen that the model results are of about the right size but somewhat lower than the measured values. The greatest deviation is found for magnesium and calcium, where the calculated out-fluxes are less than half of the measured ones. Apart from these elements the results from the simulations seems reasonable, considering that there is some uncertainty involved in the measurements and that the actual precipitation in the measuring period is 18 % greater than the value used in the simulations.

In Table 4.8. the element content of the litterfall is shown along with the calculated ion uptake in the trees. In the rather simple forest model all uptake of ions is returned with the litterfall and thus reasonable agreement is to be expected between the measured and the calculated values.

Table 4.8. Material turn-over in the trees. The litterfall was collected in the period April 1985 - April 1986 /9/. The calculated ion uptake is from the third year of a five-year simulation.

Element	Content in litterfall (g/m^2)	Calculated ion uptake (g/m^2)
Na	0.28	0.33
Mg	0.77	0.72
K	2.07	0.79
Ca	4.99	5.58
N	4.00	2.96
S	0.49	0.67

It is seen that the litterfall is fairly well reproduced by the calculated ion uptake, but it must be remembered that the water uptake coefficients for all elements except for magnesium and calcium have been adjusted with this connection in mind. The adjustments were made on the basis of a preliminary simulation in which all uptake coefficients were set to unity. The adjustments were performed rather roughly as there was no basis for a great accuracy.

After the adjustments the calculated uptake of sodium, nitrogen and sulphur was changed in the expected way, but the uptake of potassium was only changed from 0.25 g/m^2 to 0.79 g/m^2, as the uptake coefficient was increased by a factor of ten.

The reason for this is that increased uptake of potassium in a time step would exceed the total amount dissolved in the soil water. This problem can be solved by increasing the number of time steps per year (at present the maximum number is 12) or through changes in the soil chemistry model, e.g. inclusion of weathering of K-containing silicates. In order to illustrate the influence of the number of time steps it can be mentioned that in a similar simulation with only one time step per year the calculated uptake of potassium was reduced to less than a third of the amount calculated with 12 time steps per year.

4.3.2. Comparison of measured and calculated soil water concentrations.

At the experimental site water samples was collected with lysimeters at a depth of 40 cm and 90 cm. For comparisons with these samples, 5-year simulations with one-month time-steps have been run. Layer 2 and 4 in the simulations corresponds to the samples from 40 cm and 90 cm respectively. In Table 4.9 the measured and calculated soil water concentrations are shown.

Table 4.9. Measured and calculated soil water concentrations. The experimental values are averages of samples from the period November 1985 - June 1987 (Bille-Hansen, personal communication). The ECCES results are taken from the last year of a 5-year simulation.

Element	Measured (mMmol/l)		Calculated (mMol/l)	
	40 cm	90 cm	layer 2	layer 4
Ca^{2+}	0.49	0.59	0.44	0.45
Mg^{2+}	0.047	0.15	0.085	0.10
Na^{+}	0.34	0.29	0.44	0.43
K^{+}	0.0089	0.0064	0.014	0.0035
NO_3^{-}	0.20	0.25	0.54	0.34
Cl^{-}	0.41	0.42	0.36	0.36
SO_4^{2-}	0.29	0.27	0.32	0.36
Al^{3+}	0.0016	0.0017	0.00028	0.00018
Zn^{2+}	*	*	0.00019	0.00019
pH	5.88	6.00	5.77	5.95

* There was a wide variation in the measured Zn-concentrations. The main part of the values were in the range 0.00015-0.00030 mmol/l.

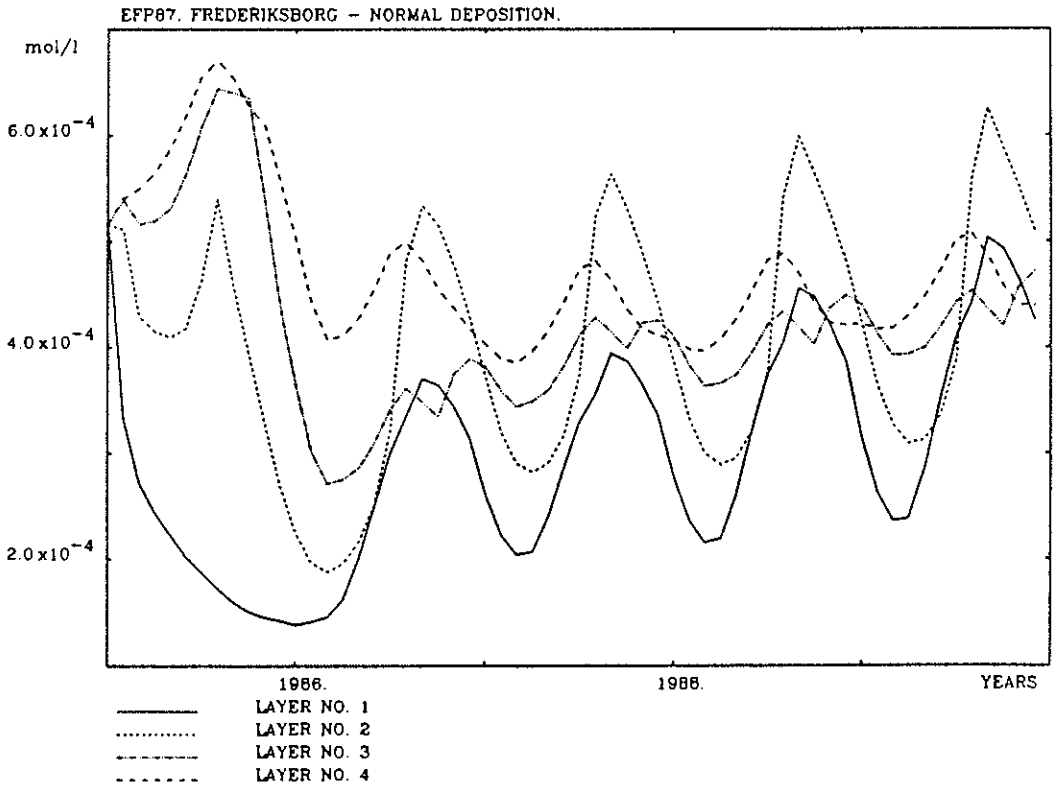

Fig. 4.2. Short term variation in calcium concentration in the soil water for the four layers.

When comparing the results it has to be taken into account that the output from the model simulations is the calculated concentrations before uptake of ions to the trees. This means that the actual concentrations for ions with an uptake coefficient larger than one will be somewhat lower.

It can be seen that the calculated concentrations generally are in fair agreement with the measured concentrations. However, there are some exceptions:

- For magnesium and potassium the calculated concentrations for layer 2 are too high while the concentrations for layer 4 are on the low side. This is probably a result of the simplistic description of material cycling in the model. Some of the same effect is seen for nitrogen.

- The calculated aluminium concentrations are about an order of magnitude too low and this suggests that the aluminium description should be improved.

In Fig. 4.2. a plot of the calculated calcium concentration is shown in order to illustrate the variation. It is clearly seen that the first year, in which there is no input from decomposition of organic matter, differs significantly from the rest. It is also seen that the largest variation is found in the upper layers, which are most influenced by deposition, litter decomposition and uptake in trees.

4.3.3. Long-term simulations.

In order to investigate the long-term development in the soil at the experimental site, simulations of a period of 30 years have been performed with the above mentioned data.

As an example of how the soil would respond to a serious SO_2-pollution, a simulation was also performed in which the deposition of SO_2 (and the corresponding proton production) was assumed to be five times as high. This simulation was extended to a period of 100 years so that some of the more dramatic effects could be seen.

4.3.3.1. Expected long-term development at the experimental site

Figure 4.3. shows the pH development in the different soil layers. It can be seen that the upper layer is somewhat influenced by the acid deposition, while the lower layers are still dominated by the CO_2/HCO_3^- system.

This observation is confirmed by Fig. 4.4, which shows the base saturation. The base saturation for the upper layer decreases from about 0.97 at the start to about 0.75 at the end of the simulation, while it remains near unity in the other layers throughout the whole period.

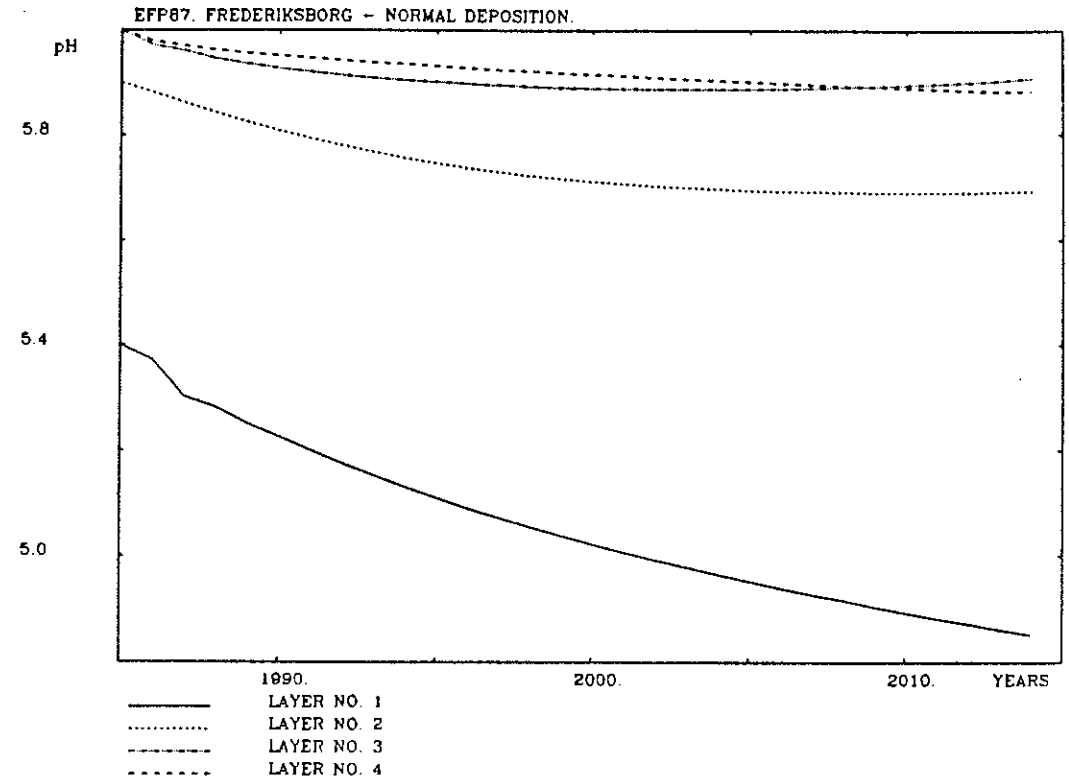

Fig. 4.3. Calculated pH in the soil water for the four layers.

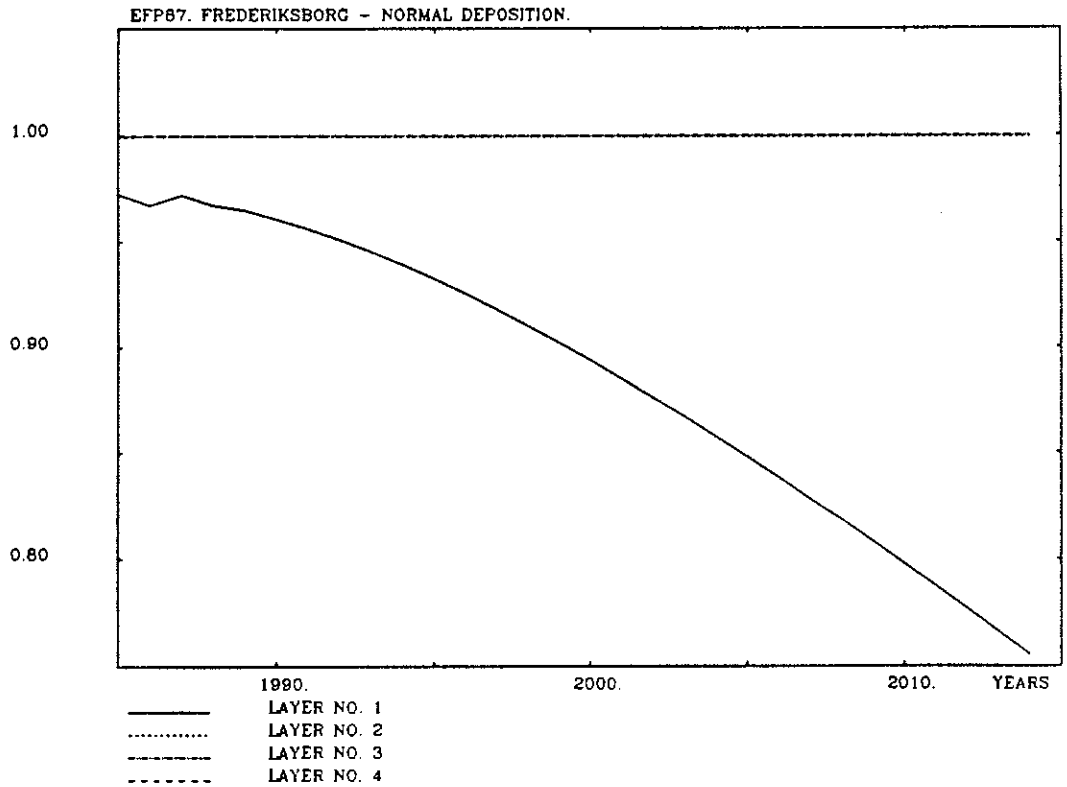

Fig. 4.4. Base saturation for the four layers. Only the upper layer, No. 1, is showing decreased base saturation under the assumed circumstances.

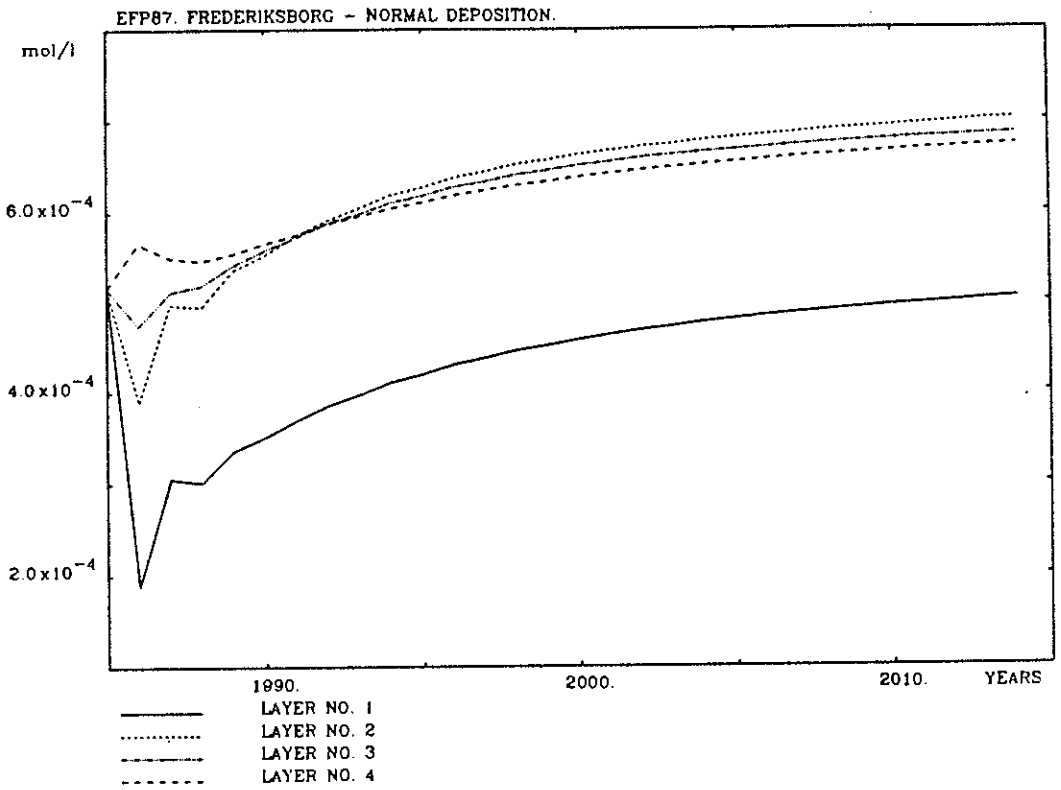

Fig. 4.5. Calcium concentration in the soil water for the four layers.

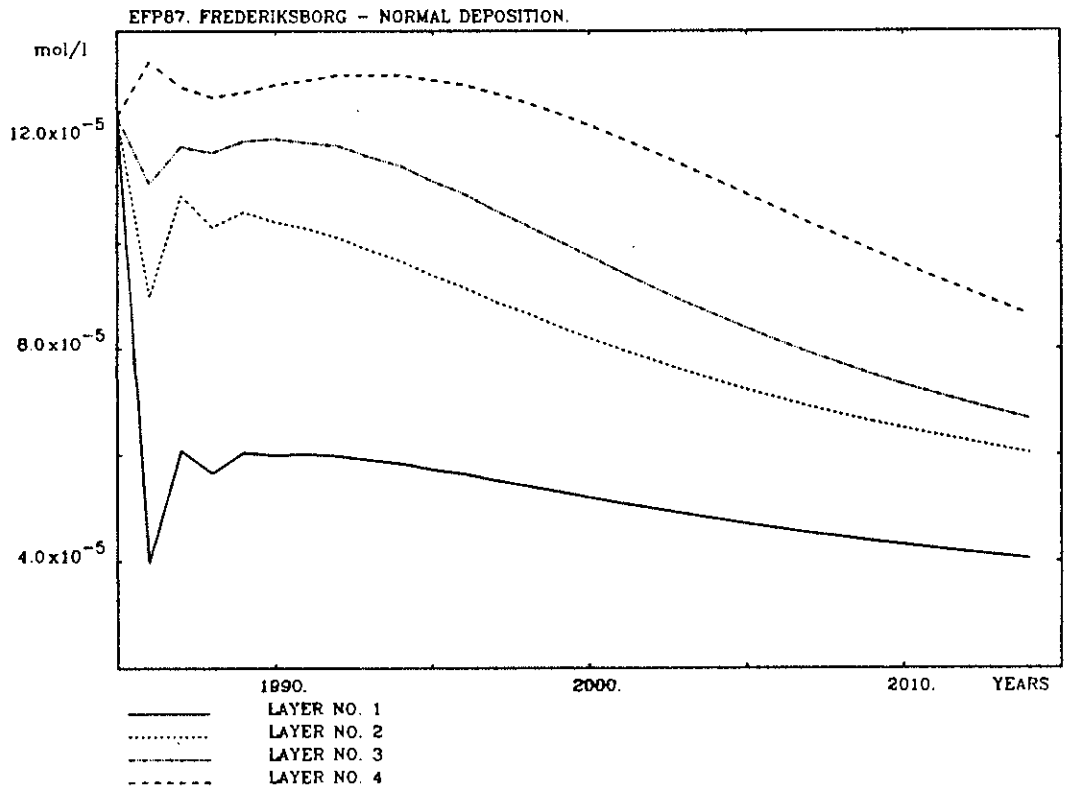

Fig. 4.6. Magnesium concentration in the soil water.

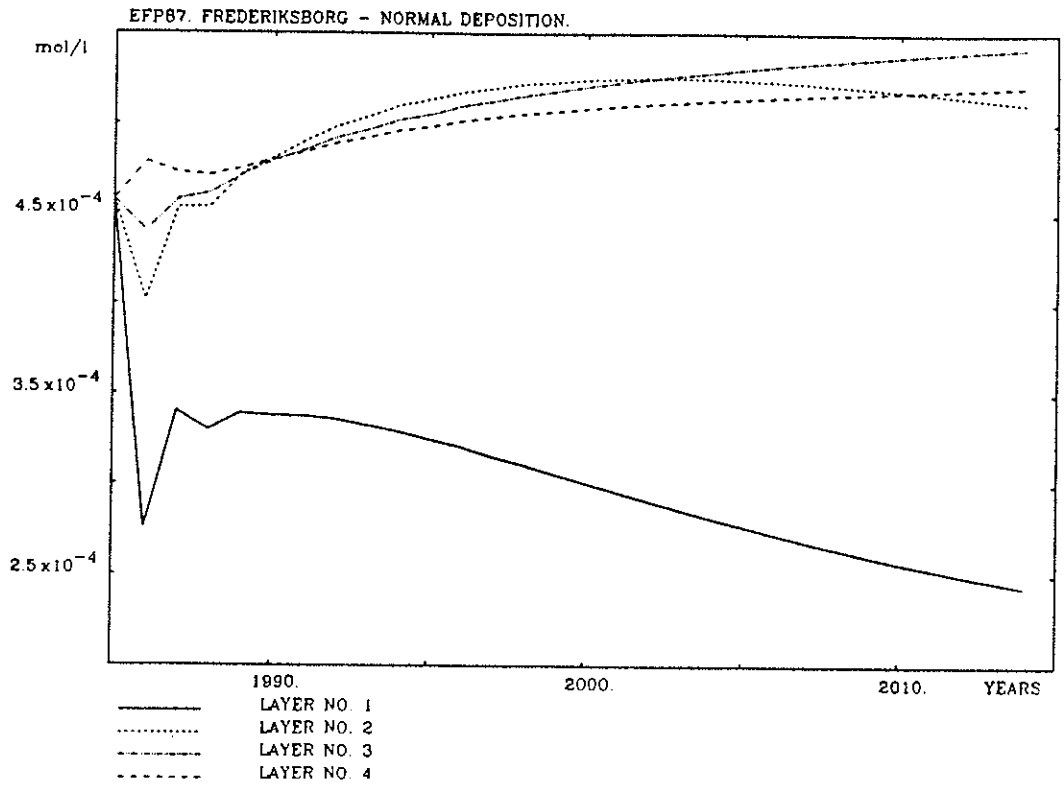

Fig. 4.7. Sodium concentration in the soil water.

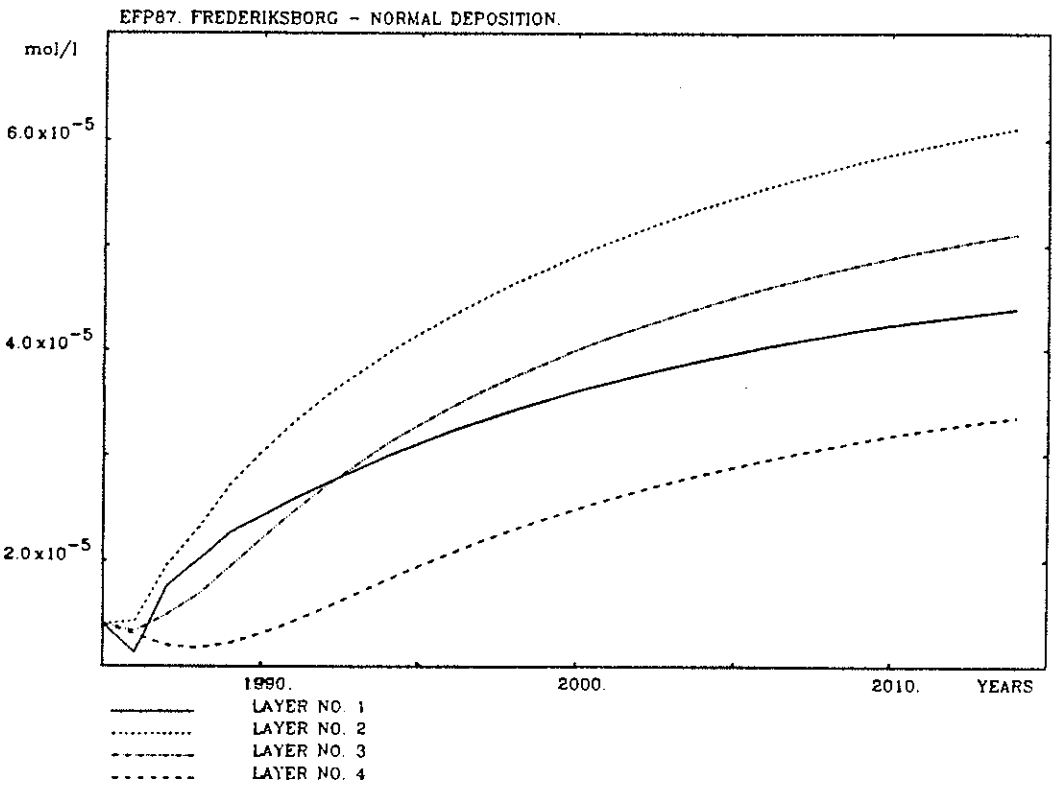

Fig. 4.8. Potassium concentration in the soil water.

In Figs. 4.5. to 4.8. concentrations in the soil water are shown for some of the macro-ions. It can be seen that, apart from potassium, the concentrations in the upper layer are significantly lower than in the rest of the layers as a consequence of the lower pH in the upper layer. With the exception of magnesium and, to a lesser extent sodium, all concentrations are increasing throughout the simulated period.

The different direction of the curves is a consequence of the differences in the distribution and the water-uptake coefficients. For instance, the large increase in potassium concentration is a result of the postulated high uptake of potassium, which leads to a recycling of this element with almost no leaching from the root zone.

4.3.3.2. Long-term development at a SO_2-polluted site.

In Fig. 4.9. showing the development in pH for the SO_2-polluted case some more dramatic effects are demonstrated. The major buffering effect above pH 4 is related to the variable cation exchanger and is due to hydrogen ion consumption when the weak ion exchange sites are converted into the undissociated form. Below pH 4 soil buffering is much less efficient, resulting in the sharp decrease in soil pH seen for the upper layer, until at a somewhat lower pH the buffering via dissolution of $Al(OH)_3$ takes over.

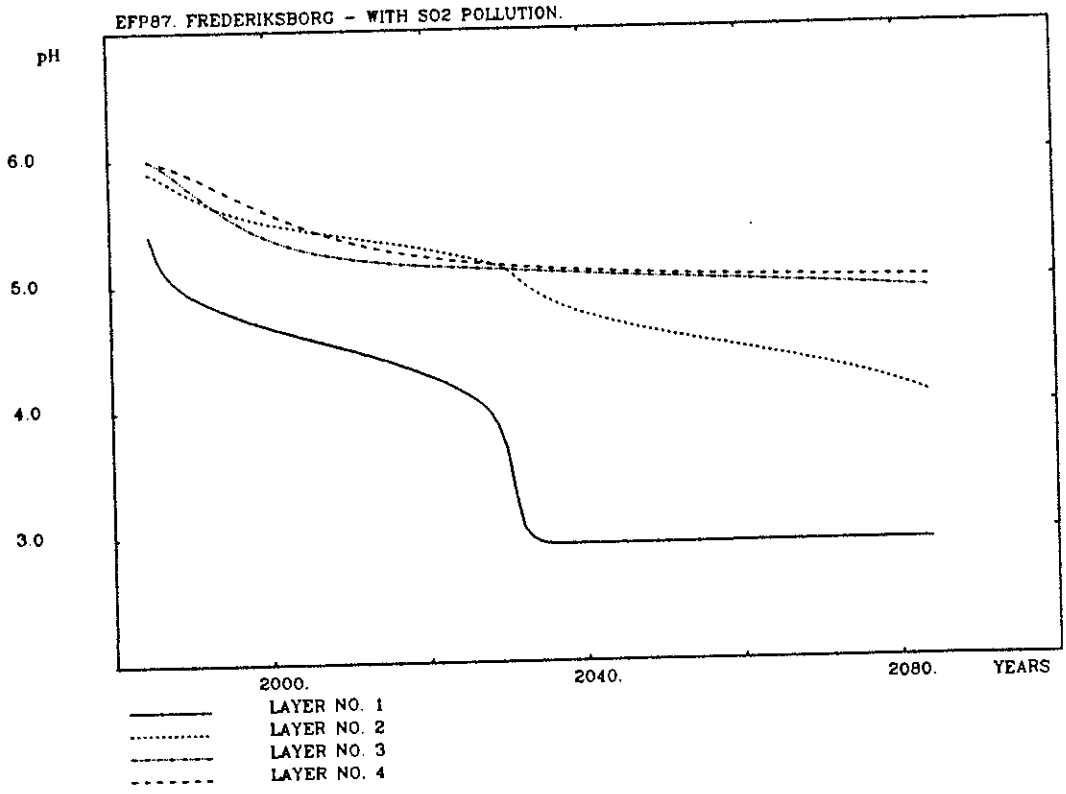

Fig. 4.9. pH in the SO_2-polluted case.

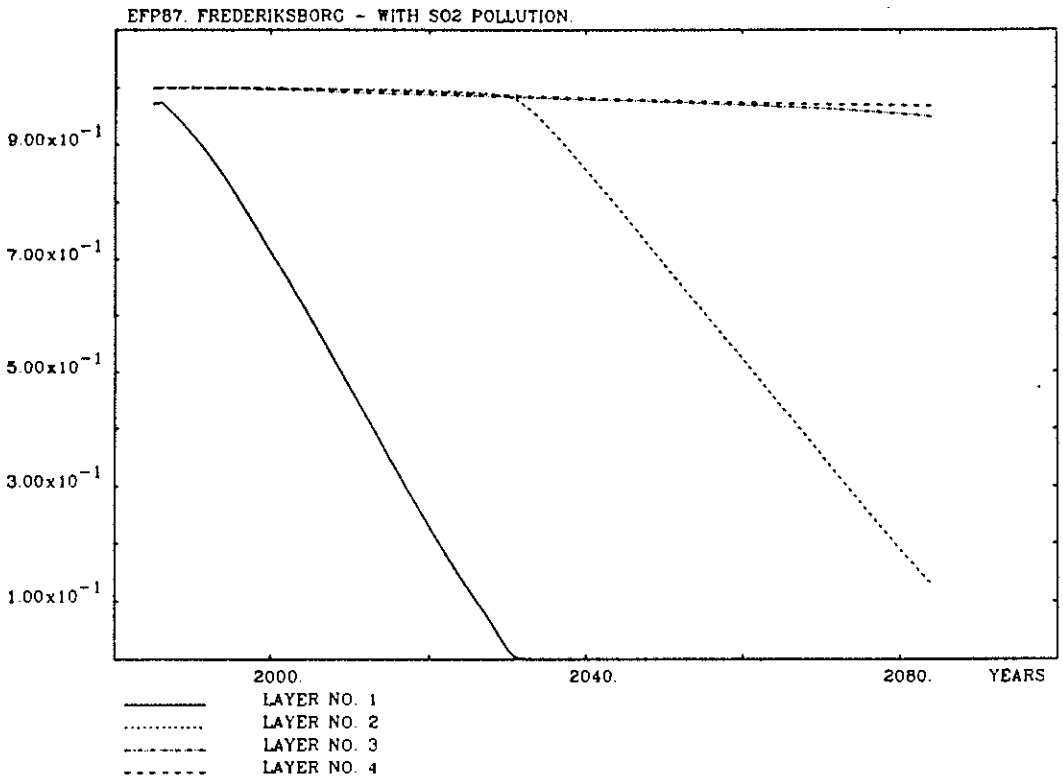

Fig. 4.10. Base saturation in the SO_2-polluted case.

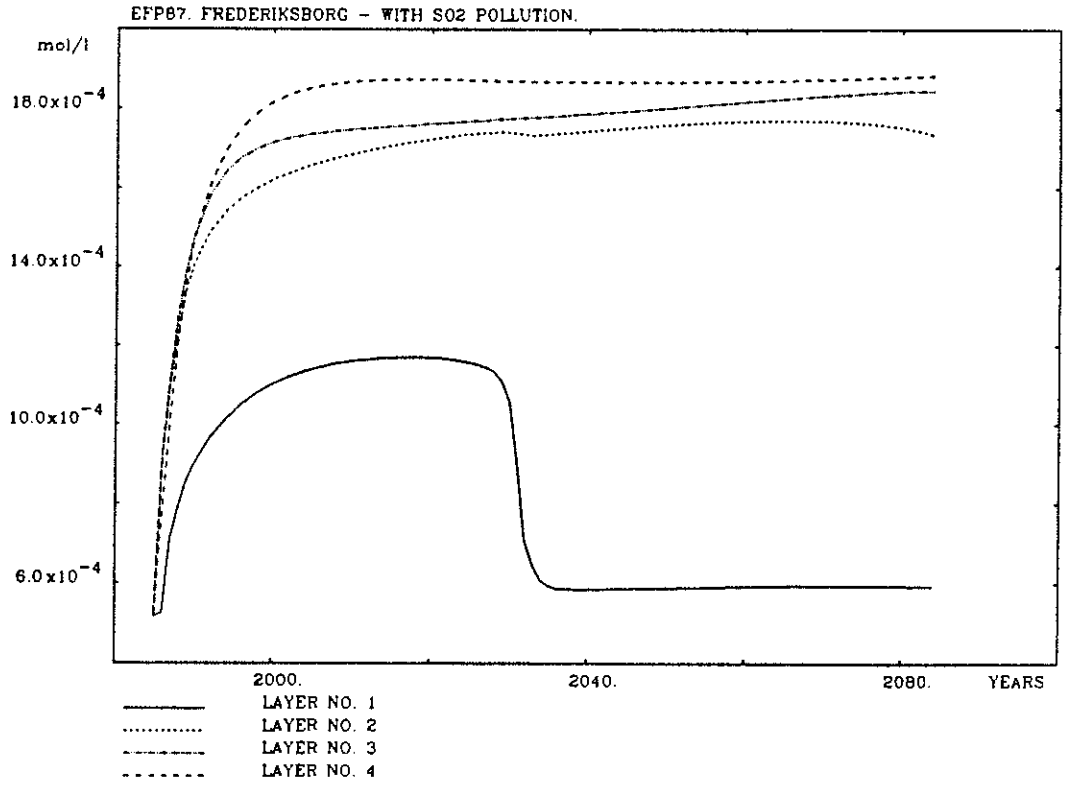

Fig. 4.11. Calcium concentration in the SO_2-polluted case.

The corresponding development in the base saturation is shown in Fig 4.10. It is seen that the base saturation in one layer is almost completely exhausted before the decline in the next layer sets in. This, of course, is an artefact of the use of four separate soil layers in the model.

As an example of the development in the soil solution the concentration of calcium is shown in Fig. 4.11. It is seen that until a certain point there is an increase in the concentration during the exhaustion of the cation exchanger. When the cation exchanger is completely exhausted there is a sharp decrease in the concentration to the level found in the rainwater.

4.4. Validation discussion.

The monitoring programme has given a very wellcome opportunity to use the ECCES-model in connection with consistent data from a real forest system. With these data the model has shown up to be well behaved and to produce reasonable results in most respects. However, despite the fact that the time-scale of the monitoring programme has been too short to allow firm conclusions about the model qualities, there seems to be some areas in which the model could be improved:

- The calculation of ion uptake in trees is inaccurate for ions with large uptake coefficients.
- The calculated aluminium concentrations in the soil water are inaccurate, but methods for improvements are available.
- The modelling of nitrogen compounds in the soil is too simple but improvements would probably require a more advanced hydrology model.
- Buffering effect and cation supply from weathering of silicate minerals are not included.
- Facilities for initiating a calculation are too primitive, giving rise to unrealistic oscillations in the beginning.
- Variations in climatic conditions (rainfall etc.) are difficult to introduce.
- Facilities for sensitivity and uncertainty evaluation should be included.

Some of these features will be remediated in a PC-version of the soil chemistry model which is under implementation.

5. GENERAL CONCLUSIONS

Validation and further development of the forest and forest soil-chemistry models within the frame of the ECCES system is the primary purpose of the excercise described in the present report. However, due to manpower limitations and some unexpected analytical difficulties this has only been partially successful. Interesting results were obtained on the following topics:

- Work done by SFF and DMU /3/ outside the present project has resulted in extensive data sets for the turn-over of macro-components (S,N Ca,Mg,K,Na,etc.) in a beech stand on a clayey soil in an area with low air pollution. The data - or closely related data - were used as input and control for calculations with the ECCES model. Reasonable agreement between calculations and measured values could be attained as shown in Section 4. However, model sensitivity to data variation and to some reasonable alteration in model structure has not been tested and a true validation case has therefore not been established. Comparison with results from other sites and other exposure conditions should also be made. An inherent difficulty is that time series of deposition data, soil solution analyses, etc. probably always will be very short. A direct validation of calculations covering long periods can therefore not be made.

- However, using the model as it presently is, it was shown that major changes in soil pH will be slow for this high ion-exchange capacity soil even if deposition of acidifying components is increased considerably. In reality the development will be even slower since the present soil model does not take for example weathering of feldspar minerals into account.

- As far as microelements are concerned data sets for heavy metals in precipitation, throughfall and litterfall were collected within the present project. The litter analyses - for beech as well as spruce - are similar to results obtained elsewhere, see Section 3.2, although the Zn turn-over appears rather high. The analyses for heavy metals in soil water samples were uncertain due to extremely low concentrations. However, the orders of magnitude are what can be expected for this unpolluted soil with relatively high pH.

- Soil samples typical for the site were collected at 5 different levels (0-5, 5-25, 30-45, 55-75, 90-110 cm) and characterized in the laboratory. The pH varied from ~5.4 to 6.0 down through the layers. Also the content of clay increased, while the organic content decreased. This is reflected in a decrease with increasing depth of the pH-dependent part of the ion exchange capacity of the soil. This was included in the test calculations.

- Experimental studies of Cd and Zn adsorption in competition with Ca were also made and have given an improved understanding of the possibilities for modelling the soil water concentrations of these elements. Exponential expressions of the Freundlich type are presumably the most easy to introduce into the general framework of the soil chemistry model. However, low desorption rates may make it difficult to simulate Zn concentrations found in practice. The Cd behaviour is probably better represented by a simple equilibrium model. The multi-Langmuir type of expression (see Section 3.4.3.) could also be of interest for example in the study of micro-element synergistic effects which may be relevant if only a small number of high affinity sites are present in the

soil. Due to time constraints within this project it has not been possible to develop these ideas into practical modelling, and no modelling of heavy metal behaviour has been attempted in Section 4.

- The concentration profiles for various elements down throgh the soil layers were established and show expected trends, for example with Pb much increased in the uppermost layer.

- A set of experiments with artificially accelerated extraction of soil samples with successive portions of weak sulphuric acid was also performed. Modelling of the analytical results was performed with the ECCES soil model. Time did not permit testing of some obvious improvements in the model based on these experimental results. A change in calculation of the Al-speciation is for example needed.

The general conclusion is that the participation in the study on ion-balance in a forest ecosystem has been a valuable opportunity to test the calculation ability of the ECCES models. However, the present model is rather heavy to work with and further development should preferably take place using a simpler and more flexible version. A model for PC-use is in preparation.

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DATA ACQUISITION AND APPLICATION OF THE SOIL CHEMISTRY MODEL ECCES TO FOREST SOILS

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Abstract (Max. 2000 char.)

This final report describes work done on validation of the environmental-effects modelling system ECCES as applied to forest soils. A short description is given of a site in a Danish forest district where monitoring of dry and wet deposition, throughfall, litterfall and soil water composition is continuing since 1985.

The present project is a supplement to this field investigation and has covered the following topics:

- Investigation of deposition and transport of heavy metals at the forest site. Analyses for Cd, Zn, Pb, etc. in precipitation, throughfall, litterfall and soil-water and in samples of the soil have been made using ICP-MS and other methods. The data are compared with similar data from the literature and are used to estimate the fluxes of heavy metals. The clayey soil is unpolluted and the concentrations in the soil water were mostly below the detection limits.
- Characterization of the soil to obtain data needed for the modelling of material fluxes in the system for major as well as minor elements. Cation exchange capacities as function of pH were measured for samples from four soil horizons. Distribution coefficients were determined for the Cd/Ca and Zn/Ca systems at various pH. Fitting with Langmuir or Freundlich expressions is discussed. Anion exchange capacities were low in this relatively high pH soil. Accelerated extraction of soil samples with weak sulphuric acid to obtain indications for the long-term development was also done.
- Development of a simple forest model coupled with the existing soil model and testing of the overall system using data from the field investigation and laboratory experiments. Simulation of material fluxes of major components in the forest system were in reasonable agreement with the measured values, taking some rather coarse assumptions in the model into account. Time did not permit the introduction of various improvements indicated by the experimental work. Modelling of the turn-over of heavy metals was not attempted. Example calculations simulating soil development over long periods are presented. Qualitatively the development is thought to be correct, but further work is needed to improve confidence in the results. A more flexible version of the model is under development.

The project was carried out as a cooperative effort between the Danish Forest Experiment Station (SFF), Danish National Environmental Research Institute (DMU) and Risø National Laboratory. It was supported by grants from the Danish Ministry of Energy.

Descriptors – EDB

ACIDIFICATION; AIR POLLUTION MONITORING; ARSENIC; ATMOSPHERIC PRECIPITATIONS; CADMIUM; CATIONS; COMPUTERIZED SIMULATION; DATA ACQUISITION; E CODES; FIELD TESTS; FOREST LITTER; FORESTS; ION EXCHANGE; LEACHATES; LEAD; PH VALUE; SOIL CHEMISTRY; SOILS; SULFUR DIOXIDE; ZINC

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